

Lattice Infrared Spectra of Boron Nitride and Boron Monophosphide*

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The fabrication of highly dense, highly polished compacts consolidated from monocrystalline cubic boron nitride at very high pressures and temperatures has enabled us to record the infrared reflection spectrum of cubic boron nitride from 80 to 550°K. For annealed compacts, the reststrahlen peak reflectivity of about 85% could be obtained. Analysis of data by a damped-oscillator model yields TO ($k \approx 0$): 1065 cm⁻¹, $\epsilon_0 = 7.1$, $\epsilon_\infty = 4.5$; and LO ($k \approx 0$): 1340 cm⁻¹. Infrared transmission measurements on small single crystals were obtained with a beam condenser. Eleven absorption peaks were observed between 600 and 3000 cm⁻¹. These are assigned as combinations of four Brillouin-zone boundary modes: LO 1232 cm⁻¹, TO 1000 cm⁻¹, LA 685 cm⁻¹, and TA 348 cm⁻¹. The reflection spectrum of hot-pressed compacts of boron monophosphide single crystals measured between 600 and 1000 cm⁻¹ showed a monotonic decrease of reflectivity from about 15 to 9% with an extremely weak reststrahlen band around 825 cm⁻¹. The estimated values of long-wavelength optical modes are TO ($k \approx 0$): 820 cm⁻¹, and LO ($k \approx 0$): 835 cm⁻¹. The results thus suggest an extremely low effective ionic charge (~ 0.25) for the crystal. Additional deduced physical properties of cubic boron nitride and boron phosphide are discussed.

I. INTRODUCTION

THE synthesis of cubic boron nitride from boron nitrogen catalyst systems was first announced by Wentorf¹ in 1957. The compound was subsequently obtained by direct transformation from the hexagonal form by Bundy and Wentorf² several years later. Except for some measurements in the ultraviolet region³ between 7 and 9 eV, where cubic boron nitride is reported to have strong absorption, no further optical measurements have been made to date. Optical measurements and the data derived therefrom are of great interest in the investigation of the bond strength, nature of the chemical bond, mechanical properties, and the electronic properties of cubic boron nitride particularly as related to the other III-V compounds.

Optical measurements, especially in the vibrational region of the spectrum ideally require a rather sizable specimen. The fabrication of highly dense, highly polished compacts consolidated from monocrystalline cubic boron nitride at elevated temperatures and pressures enabled us to record the infrared reflection spectrum of cubic boron nitride, from liquid-nitrogen temperatures to 550°K. These data are further supported and elaborated upon by single-crystal absorption measurements, attenuated-total-reflection (ATR) techniques, and thermal-emission spectra.

In an effort to further delineate possible regularities in the optical and other related physical properties in the III-V compounds, we have also studied the reflection characteristics of hot-pressed compacts of cubic BP in its vibrational region from 600 to 1000 cm⁻¹.

II. EXPERIMENTAL

The single crystals of cubic boron nitride used in this study were grown at very high pressures and temperatures from a catalyzed hexagonal boron nitride system. Growth parameters as well as cell and press configurations were similar to those described in the literature. For this particular application, lithium nitride was used as the catalyst. For the single-crystal measurements we employed platelet-like crystals approximately 400 μ by 600 μ and 30- μ thick. They were both nonconducting ($\rho \approx 10^{10}$ Ω -cm) and semiconducting ($\rho \approx 10^4$ Ω -cm, beryllium-doped) and transparent. No specific chemicals, other than the catalyst and dopants, were added to the growth system. The plate-like morphology was induced by the proper selection of the growth environment as well as the pressure and temperature parameters.

Reflectivity measurements have been made on composites of cubic boron nitride (compacts). Consolidation of the crystals was accomplished by placing them in an experimental high-pressure sample holder and exposing them to very high pressures and temperatures. The degree of consolidation, which was determined primarily by measuring physical properties such as density, shear and compressive strength, is temperature-dependent. Maximum consolidation occurs at a temperature close to the (BN)_c-(BN)_h equilibrium line for the particular pressure used. Temperatures in excess of this result in back conversion to the hexagonal form. The compacts used in this study are approximately 6 mm in diam, are opaque, and have a density approaching the

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¹ R. H. Wentorf, Jr., J. Chem. Phys. **26**, 956 (1957); **34**, 809 (1961).

² F. P. Bundy and R. H. Wentorf, Jr., J. Chem. Phys. **38**, 1144 (1963).

³ H. R. Phillip and E. A. Taft, Phys. Rev. **127**, 159 (1962).

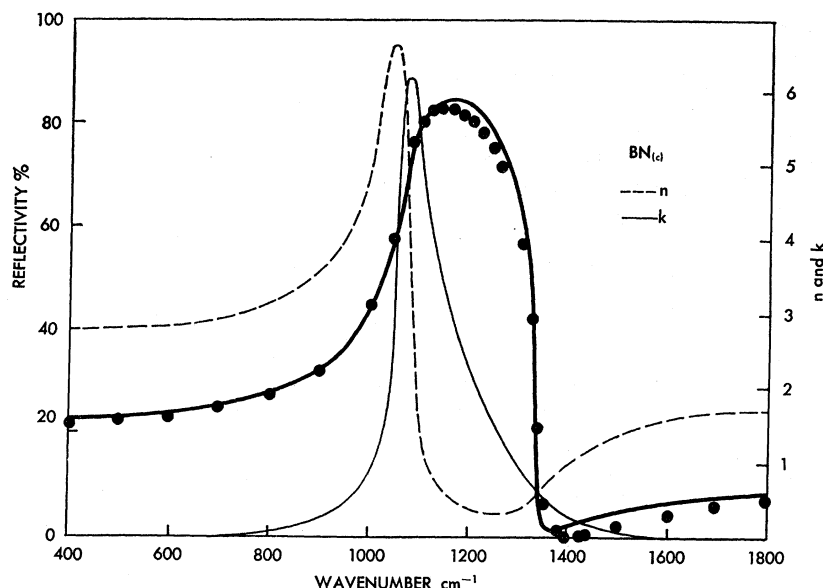


FIG. 1. Reflectivity and optical constants of cubic boron nitride.

theoretical value of 3.50 g/cc. The compacts were ground and polished on one side with successively finer diamond powder to a perfectly flat, homogeneous mirror-like finish.

Compacts of boron phosphide were made using techniques and experimental parameters similar to those described for boron nitride in the previous paragraph. As a starting material we used very fine-particle-size single-crystal boron phosphide which had been prepared by Post⁴ by direct union of the elements in evacuated sealed silica tubes for 12 h at 1000°C. The x-ray diffractometer pattern showed the material to be essentially cubic boron phosphide with a few percent of graphite of undetermined origin. After the compaction, the diffraction pattern showed again cubic boron phosphide.

In addition to compacting the boron phosphide, we have also been able to grow fairly large (1 mm across) clear single crystals of boron phosphide which are contained in the compacted matrix. So far the reports on single-crystal boron phosphide have described the crystals as reddish brown to black. More work on the exact effects of high pressure and temperature on the growth of cubic boron phosphide is in progress. Polishing the boron phosphide compacts proved more troublesome than for those prepared from boron nitride and we have never obtained as high a polish as we did on the latter.

The spectra were recorded from 400 to 2000 cm^{-1} with Perkin-Elmer Model 521 and 221 infrared spectrophotometers and appropriate reflection attachments, accessories for attenuated total reflection measurement and a 6X beam condensor for the single-crystal measurements.

III. SPECTRAL MEASUREMENTS

A. Cubic Boron Nitride

The reflectivity of cubic boron nitride (Fig. 1) is nearly constant at 22% on the low-wave-number side ($<400 \text{ cm}^{-1}$), increases to 25% at 700 cm^{-1} , while the maximum reflectivity is 84% at 1150 cm^{-1} . A sharp reflection minimum of 0.6% occurs at 1370 cm^{-1} . The reflectivity increases thereafter and becomes nearly constant with a value of 10.5% in the higher-energy side ($>1600 \text{ cm}^{-1}$). No side structure or shoulder is indicated at the higher-frequency side.

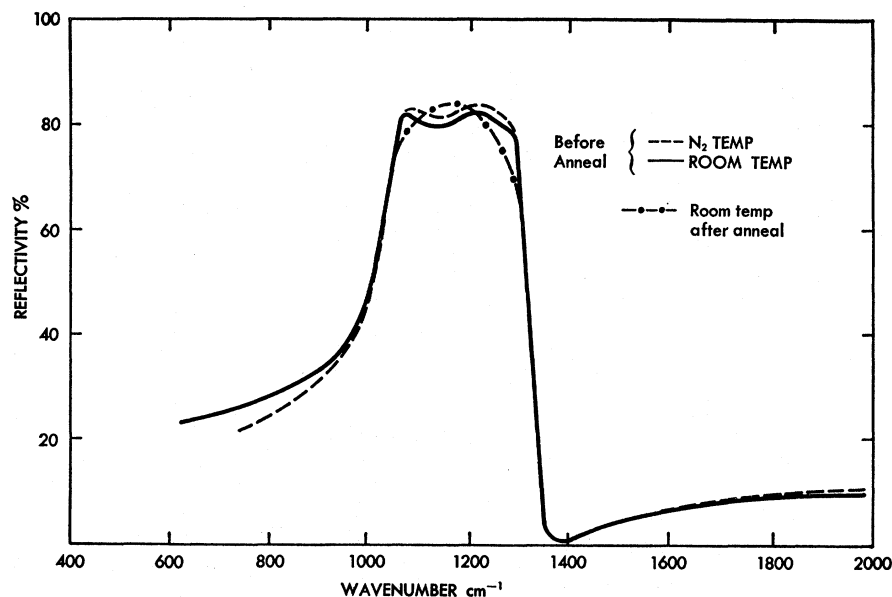
Our original measurements on the compacted boron nitride sample indicated the possibility of some minor structure in the area of maximum reflectivity (Fig. 2). Measurements at liquid-nitrogen temperatures did not resolve the structure any further and only showed an increase in maximum reflectivity of about 2% with very slight narrowing and a possible minor shift of the spectrum to higher frequencies, attesting to an extremely tightly bonded structure. Thermal anneal in air at 350°C for about 15 min only, completely eliminated the structure in the main band, which appears to have originated from surface conditions (see Fig. 2). Spectrum taken at 550°K showed a decrease in reflectivity by 4% at the maximum and about 1% at the extremities. As anticipated, the spectrum also shifted to lower wave numbers by 12 cm^{-1} . The reststrahlen spectrum is typical of an ionic crystal, and its temperature dependence is indicative of a strongly bonded crystal.

The reflection spectrum has been analyzed by means of classical oscillator theory, the details of which have been described elsewhere.⁵

⁴ B. Post, *Acta Cryst.* **11**, 310 (1958).

⁵ S. S. Mitra and P. J. Gielisse, *Progress in Infrared Spectroscopy* (Plenum Press, Inc., New York, 1964), Vol. 2, pp. 47-125.

FIG. 2. Reflectivity of cubic boron nitride under various conditions.



The cubic boron nitride belongs to the zinc-blende structure with three optical branches, of which the transverse optical (TO) branch at $\mathbf{k} \simeq 0$, where $\mathbf{k}$ denotes wave vector, gives rise to the first-order infrared activity.

The near normal reflectivity is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \quad (1)$$

where the refractive index n and the extinction coefficient k are obtained from the real and imaginary parts of the complex dielectric constant

$$\epsilon' = n^2 - k^2 = \epsilon_\infty + 4\pi\rho\nu_0^2 \frac{\nu_0^2 - \nu^2}{(\nu_0^2 - \nu^2)^2 + \gamma^2\nu^2\nu_0^2}, \quad (2)$$

$$\epsilon'' = 2nk = 4\pi\rho\nu_0^2 \frac{\gamma\nu\nu_0}{(\nu_0^2 - \nu^2)^2 + \gamma^2\nu^2\nu_0^2}, \quad (3)$$

where ϵ_∞ is the high-frequency limiting value of the dielectric constant, ν_0 is the Brillouin-zone center ($\mathbf{k} \simeq 0$) transverse optical mode frequency, $4\pi\rho$ is the strength of the resonance and γ the width or the damping constant. The damped-oscillator calculation of the reststrahlen band was accomplished with the aid of a computer (IBM 7090). Good agreement between calculated and observed reflectivity is obtained by assuming a single resonance for which the following parameters were used: $\epsilon_\infty = 4.5$, $4\pi\rho = 2.6$, $\nu_0 = 1065 \text{ cm}^{-1}$, and $\gamma = 0.038$. The static dielectric constant ϵ_0 is given by $4\pi\rho + \epsilon_\infty = 7.1$. The calculated reflectivity [from Eq. (1)] is compared with the observed values in Fig. 1. The optical constants n and k are also given in Fig. 1.

The zone-center longitudinal optical mode ν_l , when identified with the high-frequency minimum in reflectivity, has a value of 1370 cm^{-1} , which is in fairly good agreement with the value obtained from the Lyddane-Sachs-Teller relation.⁶

$$\nu_l(\epsilon_0/\epsilon_\infty)^{1/2}\nu_0 = 1340 \text{ cm}^{-1}.$$

In the visible region, the refractive index may, as a first approximation, be calculated from $n^2 = \epsilon_\infty$, which gives a value lower than that estimated by Wentorf⁷ in his early observations shortly after his synthesis of cubic boron nitride. The value estimated at that time was 2.22, which would give $\epsilon_\infty = 4.93$. We have redetermined the index of refraction in the visible region by the so-called Beche⁸ method involving the matching of the indices of the boron nitride and carefully prepared melts of sulfur and selenium at 10% weight intervals. The variation of the index of refraction with composition of the melts at various wavelengths have been determined by Merwin and Larsen.⁹ A standard Zeiss polarizing microscope equipped with a continuous interference filter which converted the tungsten source light into light of the desired wavelength was used. The measurements were made under 200-power magnification at room temperature. The results are plotted on a Hartmann dispersion net and are shown in Fig. 3. As anticipated, the boron nitride crystals show a high dispersion in the visible. Using the conventional expression for relative dispersion,

$$V = (N_F - N_C)/(N_D - 1),$$

where N_F , N_C , and N_D stand for the indices at the

⁶ R. H. Lyddane, R. G. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).

⁷ R. H. Wentorf, Jr., *J. Chem. Phys.* **36**, 1990 (1962).

⁸ E. E. Whalstrom, *Optical Crystallography* (John Wiley & Sons, Inc., New York, 1960).

⁹ H. E. Merwin and E. S. Larsen, *Am. J. Sci.* **34**, 42 (1912).

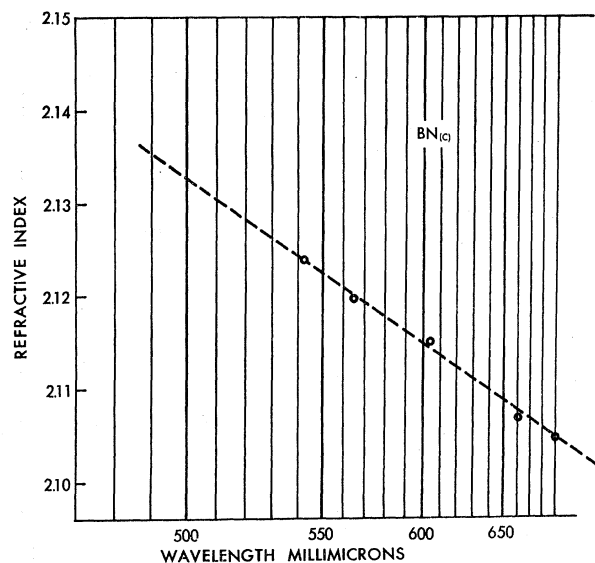


FIG. 3. Refractive index of cubic boron nitride in the visible region.

Fraunhofer *F*, *C*, and *D* wavelengths, we obtain a dispersion of 0.0377 which is close to but less than that of diamond. The value of the index of refraction of cubic boron nitride for sodium light at 589.3 mμ may be estimated at 2.117, which gives $\epsilon_{\infty} \approx 4.48$, in close agreement with 4.5 obtained from our damped oscillator analysis.

Transmission measurements on powder samples dispersed in acetone are shown in Fig. 4 for increasing concentrations of boron nitride. A maximum occurs at approximately 1075 cm⁻¹, which may be identified with the fundamental absorption, as well as a sharp minimum at 1365 cm⁻¹, in agreement with the results for the reflectivity measurements. At higher wave numbers the absorption rises again, probably owing, for the most part, to particle scattering.

The thermal emission as compared to a global source plotted as a function of frequency qualitatively shows the inverse of the reflection spectrum between 350 and 550°K, and indicated the expected temperature dependence of the reststrahlen spectrum.

Attenuated total reflection spectrum showed some structure in the two-phonon region and a sharp minimum at about 1350 cm⁻¹.

Infrared transmission measurements were also made on small single-crystal platelets of undoped as well as semiconducting cubic BN. Figure 5 shows about 11 peaks in the region between 600 and 3000 cm⁻¹ for the undoped material. This absorption is attributed to multiphonon absorption and assigned to combinations of four Brillouin zone boundary modes: LO 1232, TO 1000, LA 685 and TA 348 cm⁻¹. The possibility of impurity bands should not be excluded but has not been fully investigated at this time. The observed frequencies and their assignments are tabulated in Table I.

TABLE I. Observed frequencies and assignments for cubic BN. LO 1232 cm⁻¹; TO 1000 cm⁻¹; LA 685 cm⁻¹; TA 348 cm⁻¹.

Observed cm ⁻¹	Assignment	Expected cm ⁻¹
650	TO-TA	652
700	2 TA	696
1000-1260	reststrahlen	...
1370	2 LA (TO+TA)	1370 (1348)
1580	LO+TA	1580
1830	...	...
1920	LO+LA	1917
2000	2 TO	2000
2230	LO+TO	2232
2465	2 LO	2464
2700	2 TO+LA	2685

The region between 1000 and 1260 cm⁻¹ is entirely opaque because of the reststrahlen absorption. No obvious assignment could be made for the 1830-cm⁻¹ band. Because of the very sharp absorption, it could possibly be an impurity band.

We have expressly looked for any indication of interstitial hexagonal boron nitride formed by back conversion processes during compacting. Recent investigations¹⁰ on the properties of pyrolytic hexagonal boron nitride indicate major reflectivity maxima at 767, 1367 and 783, 1510 cm⁻¹ for $E_{\perp c}$ and $E_{\parallel c}$, respectively. Especially at the high-frequency side where the reflectivity of the cubic form of boron nitride does not rise to more than about 4%, the presence of significant amounts of hexagonal boron nitride should, but does not seem to be, indicated. Debye-Scherrer patterns taken in our laboratory on cubic boron nitride compacts have, on occasion, shown one extraneous line the 2θ value of which coincides with the (002) diffraction line of hexagonal boron nitride.

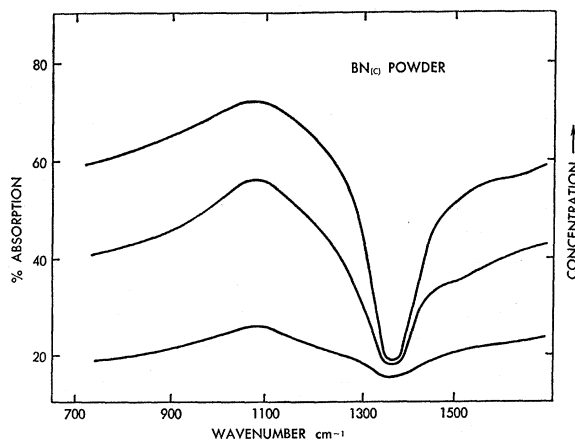


FIG. 4. Transmission spectrum of cubic boron nitride dispersed in acetone, at various concentrations.

¹⁰ G. Rupprecht, P. H. Smakula, R. Geick, and C. H. Perry, in *Molecular Structure and Spectroscopy Symposium*, Ohio State University, Columbus, Ohio, 1965 (unpublished) and R. Geick, C. H. Perry, and G. Rupprecht, *Phys. Rev.* **146**, 543 (1966).

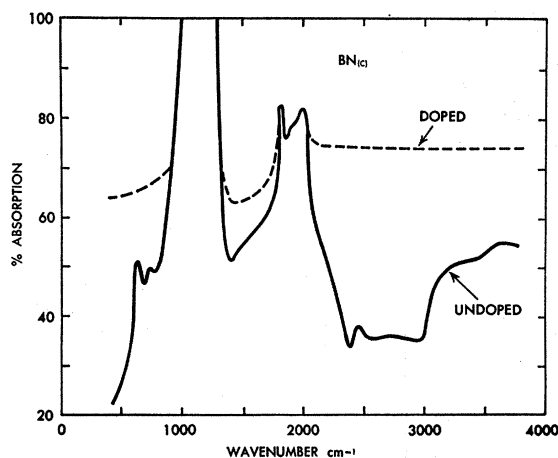


FIG. 5. Absorption of single-crystal cubic boron nitride.

B. Cubic Boron Phosphide

Cubic boron monophosphide has the same cubic zinc-blende-type structure as cubic boron nitride, a high hardness which should be greater than that of silicon carbide, and has been synthesized as a *p*-type and *n*-type semiconductor. Early predictions¹¹ gave values as high as 6 eV for the band gap of boron phosphide which induced the investigations of possible injection electroluminescence in the compound. The results¹² of such studies have led to the conclusion that the band gap might be only 2 eV. Empirical predictions mostly based on relations between bond lengths or bond strength and energy gap, varied widely, but in all cases gave values higher than 2 eV. An explanation may be the fact that in contrast to most of the other III-V compounds which have an appreciable ionic character, boron phosphide is very much covalent, as may be seen from its electronegativity difference of 0.1 eV. It may thus be argued that boron phosphide cannot be expected to take its place in the otherwise straightforward

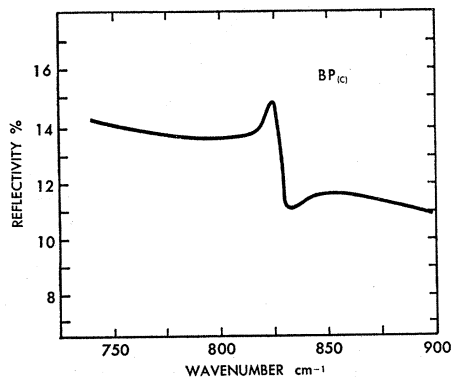


FIG. 6. Reflectivity of cubic boron monophosphide in its vibrational region.

¹¹ B. D. Stone and D. Hill, Phys. Rev. Letters 4, 282 (1960).

¹² R. J. Archer, R. Y. Koyama, E. E. Loebner, and R. C. Lucas, Phys. Rev. Letters 12, 538 (1964).

progression which is observed when the related physical properties of the other III-V compounds are compared. The ionicity of a compound, as a result of the difference in electronegativity of the participating elements, is expressed in the optical properties of the compounds. More specifically, in the lattice vibrational region, where the presence of a strong reststrahlen band and appreciable difference of the TO and LO frequencies indicate high ionicity, Wang, Cardona, and Fischer¹³ tried to obtain the reststrahlen spectrum of boron phosphide and contributed their failure to the almost completely covalent character of the compound.

Figure 6 shows the results of our reflectivity measurements in vibrational region of boron phosphide between

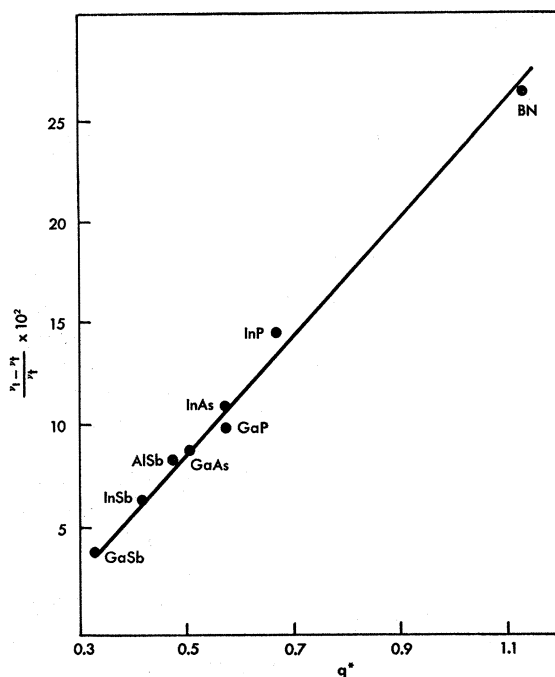


FIG. 7. Effective ionic charge q^* versus the difference between the longitudinal and transverse optical frequencies for the III-V compounds.

approximately 600 and 1000 cm^{-1} . The reflectivity monotonically decreases from about 15 to 9% except for an extremely weak, but sharp and quite distinct peak around 825 cm^{-1} , no more than 5% above the high-frequency background. The estimated values of the optical modes of lattice vibration are TO ($k \approx 0$) = 820 cm^{-1} and LO ($k \approx 0$) = 834 cm^{-1} , as identified with the reflection minimum. These results agree quite well with the strong absorption of boron phosphide polycrystalline film¹¹ at about 12 μ and the indirect determination of the TO phonon at 12.1 μ from edge emission separation.¹²

The results thus suggest an extremely low effective ionic charge for cubic boron monophosphide.

¹³ C. C. Wang, M. Cardona, and A. G. Fischer, RCA Rev. 25, 159 (1964).

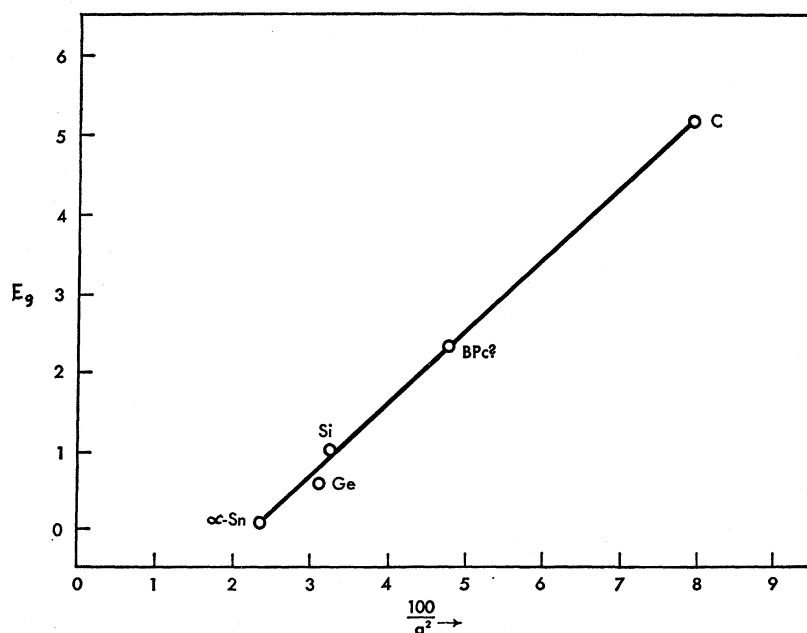


FIG. 8. Bandgap versus reciprocal of the cell edge for the group IV elements. (See text for explanation of BP position.)

IV. DISCUSSION

It is often said that cubic boron nitride, which is structurally analogous to diamond and shares many of its physical properties, is also very similar to diamond in bond character. The hexagonal form of carbon and boron nitride, although structurally similar, show important differences. Graphite is black and a good electrical conductor, while the hexagonal form of boron nitride is white and an excellent dielectric. Differences also seem to be pronounced in the case of high-pressure phases of C and BN.

The amount of ionic character, as approximated according to Pauling¹⁴ by

$$1 - \exp\left[-\frac{1}{4}(X_a - X_b)^2\right],$$

where X_a and X_b are the electronegativities of the participating atoms, indeed suggests ionic character of 22% for boron nitride. Whereas diamond forms a strong covalent bond through sharing of its electrons, cubic boron nitride thus appears to depend to an appreciable extent on electrostatic interaction for its bond energy.

It is therefore of interest to determine, by other means, the ionic character of the bond. One measure is the so-called effective charge q^* on the atom which, according to Szigeti,¹⁵ may be calculated from the dielectric constants and the long-wavelength TO mode as follows:

$$q^* = 2\pi\nu_t \left(\frac{\epsilon_0 - \epsilon_\infty}{4\pi} \right)^{1/2} \left(\frac{3}{\epsilon_\infty + 2} \right) \left(\frac{\mu V_a}{e^2} \right)^{1/2},$$

where μ is the reduced mass per unit cell, V_a is the unit cell volume and, e is the electronic charge. The q^* for cubic boron nitride is found to be 1.14, a value which is highest for all known III-V compounds. Mitra¹⁶ has shown that for these compounds the difference between the longitudinal and transverse optical frequencies, near the Brillouin zone center, increases with ionicity. Figure 7 shows a plot of $(\nu_l - \nu_t)/\nu_t$ versus q^* for the

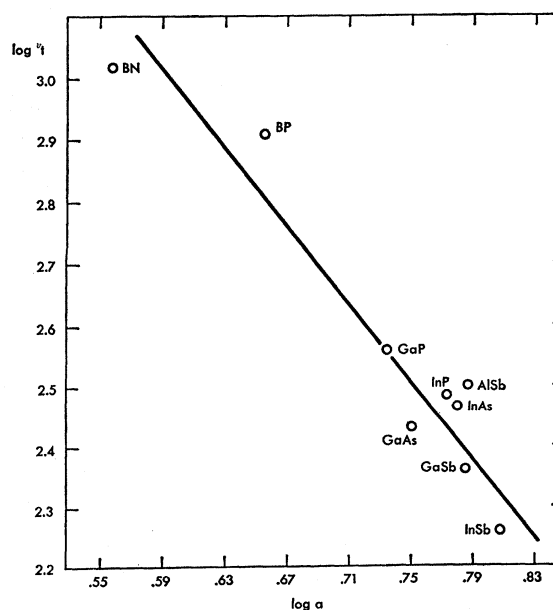


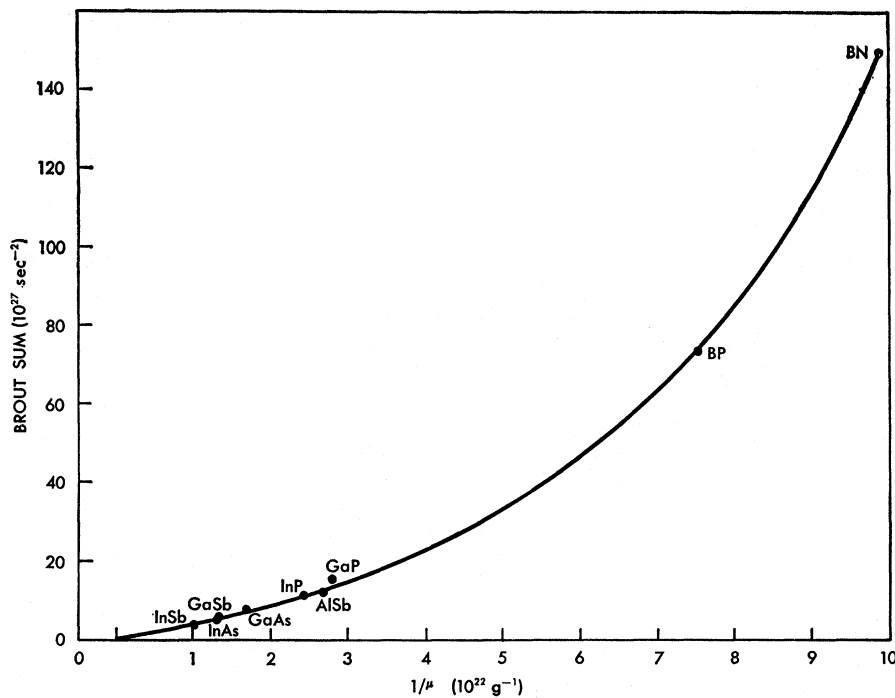
FIG. 9. Transverse optical frequency versus lattice constant for the III-V compounds, log-log scale.

¹⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1960), p. 98.

¹⁵ B. Szigeti, *Trans. Faraday Soc.* **45**, 155 (1949).

¹⁶ S. S. Mitra, *Phys. Rev.* **132**, 986 (1963).

FIG. 10. The relation between the zone center Brout sum and the reciprocal of the reduced mass per unit cell for the III-V compounds.



III-V compounds. The effective ionic charge in boron phosphide could not be determined using the Szegedi relation, since the high- and low-frequency dielectric constants are not known with any certainty. However, the extremely weak reststrahlen spectrum suggests a very small value. Using our estimated values of ν_t and ν_l for boron phosphide, the extrapolated value of q^* is about 0.25. Thus, it appears that among all the III-V compounds thus far investigated, boron nitride is most ionic while boron phosphide presumably is most covalent. These results are supported by electronegativity differences of 1.0 and 0.1, or amounts of ionic character of about 22 and 0.7% for cubic boron nitride and boron phosphide, respectively.¹⁴

Values for the bandgap of cubic boron phosphide have been reported as high as 6.0 eV,¹¹ higher than diamond, and as low as 2.0 eV.^{12,13} Estimates have also been made with the help of empirical relations between the bandwidth and observed regularities in the physical properties of the III-V compounds.¹⁷⁻²¹ They invariably result in values much higher than those determined from optical measurements. It is of interest to note that if boron phosphide is included with the group-IV elemental semiconductors and as such is treated as an essentially covalent material, we obtain a value of about 2.2 eV for the bandgap which is close to the experimental results. An example is given in Fig. 8, where the

bandgap of the group IV elements is plotted against the reciprocal of the cell edge.²¹

If it is assumed that the vibrational frequency ν_i of the i th mode of a crystal is the function of volume alone then the Gruneisen parameter for the i th mode

$$-d \ln \nu_i / d \ln V = \gamma_i$$

is expected to be a constant, though different for different modes. Although this relation is expected to represent the volume dependence of a normal mode; e.g., ν_t of any one crystal, it is indeed surprising that it is also followed by members of a homolog. When $\log \nu_t$ is plotted against $\log a$, where a is the lattice constant, approximate straight lines are obtained for the alkali halides, II-VI compounds, and the III-V compounds. A plot for the latter is shown in Fig. 9, which also includes boron nitride and boron phosphide.

For the heavier III-V compounds, Mitra and Marshall²² had obtained a linear relation between the

TABLE II. Physical properties of cubic boron nitride.

Refractive index (sodium light)	$n = 2.117$
Lattice constant ^a	$a_0 = 3.615 \pm 0.001 \text{ \AA} (25^\circ\text{C})$
Ionic distance ^a	$r_0 = 1.57 \text{ \AA}$
Density ^a (theoretical)	$\rho = 3.48 \pm 0.03 \text{ g/cm}^3$
Thermal expansion	$\alpha \sim 3.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1} (0-400^\circ\text{C})$
Compressibility	$\beta = 0.24 - 0.37 \times 10^{-12} \text{ cm}^2/\text{dyn}$
Debye temperature	$\Theta = 1700^\circ\text{K}$
Lattice energy	$U = 3420 \text{ kcal/mole}$
Transverse optical mode frequency	$\nu_t = 1065 \text{ cm}^{-1}$
Longitudinal optical mode frequency	$\nu_l = 1340 \text{ cm}^{-1}$
Center frequency	$\nu_{ctr} = 1175 \text{ cm}^{-1}$
Static dielectric constant	$\epsilon_0 = 7.1$
High-frequency dielectric constant	$\epsilon_\infty = 4.5$
Damping constant	$\gamma = 0.038$

^a References 1 and 2; other data this work.

²² S. S. Mitra and R. Marshall, J. Chem. Phys. **41**, 3158 (1964).

¹⁷ N. Sclar, J. Appl. Phys. **33**, 2999 (1962).

¹⁸ P. Manca, J. Phys. Chem. Solids **20**, 268 (1961).

¹⁹ G. V. Samsonov and Y. B. Tithov, J. Appl. Chem. (USSR) **36**, 669 (1963).

²⁰ T. Miyauchi, J. Phys. Soc. Japan **12**, 308 (1957).

²¹ F. V. Williams, Chem. Eng. News **37**, 60 (1959).

zone center Brout sum and the reciprocal reduced mass per unit cell. When the two lighter members of the homolog, boron nitride and boron phosphide are included, although a regular curve (Fig. 10) is obtained, it is no longer linear, indicating that the nearest-neighbor force constants are considerably larger in boron nitride and boron phosphide as compared to the heavier III-V compounds. The value of the Brout sum at the zone boundary, $151.1 \times 10^{27} \text{ sec}^{-2}$, is very close to that at the zone center ($k \approx 0$).

Table II summarizes the more important physical data on cubic boron nitride. The lattice cohesive energy and Debye temperature (Θ) of Table II were estimated from the infrared spectrum.²³

The compressibility k of cubic boron nitride was calculated in five different ways and the following values obtained: from the Szigeti relation,²⁴ 0.235

²³ J. N. Plendl, Phys. Rev. **123**, 1172 (1961); **119**, 1598 (1960).

²⁴ B. Szigeti, Proc. Roy Soc. (London) **A204**, 52 (1950).

$\times 10^{-12} \text{ cm}^2/\text{dyn}$; from the Brout sum rule as applicable to the zinc-blende structure,²⁵ $0.204 \times 10^{-12} \text{ cm}^2/\text{dyn}$; from the expression connecting Θ with k due to Mitra and Joshi,²⁶ $0.246 \times 10^{-12} \text{ cm}^2/\text{dyn}$. The compressibility was also obtained from the relation between the centro-frequency and elastic constants of solids,²⁷ $0.24 \times 10^{-12} \text{ cm}^2/\text{dyn}$. A more recently derived formulation²⁸ relating the compressibility with cohesive energy and molecular volume leads to a somewhat higher value of $0.37 \times 10^{-12} \text{ cm}^2/\text{dyn}$. Since no experimental value of the compressibility of cubic boron nitride is available, the limiting values, obtained as described above, are quoted in Table II.

²⁵ R. Brout, Phys. Rev. **113**, 43 (1959), for its application to the zinc-blende structure see Ref. 22.

²⁶ S. S. Mitra and S. K. Joshi, Physica **27**, 376 (1961).

²⁷ J. N. Plendl and P. J. Gielisse, Appl. Opt. **4**, 853 (1965).

²⁸ J. N. Plendl, S. S. Mitra, and P. J. Gielisse, Phys. Status Solidi **12**, 367 (1965).

Errata

Electronic Band Structure in the Sodium Iodide Crystal, A. BARRY KUNZ [Phys. Rev. **151**, 620 (1966)]. The last line in the caption for Fig. 6 should be " $a = 6.15$ Bohr units," and the last line of the caption for Fig. 8 should be " $a = 5.98$ Bohr units."

Piezorefectivity of the Noble Metals, M. GARFINKEL, J. J. TIEMANN, AND W. E. ENGELER [Phys. Rev. **148**, 695 (1966)]. Footnote No. 22 should

read: In this notation, the dielectric-constant and strain tensors are represented by six-component vectors and W becomes a 6×6 matrix. Equation (1) is then written $\Delta\epsilon_i = W_{ij}e_j$ where i and j run from 1-6. In this equation, the first three components of strain and dielectric-constant variations are given by $e_j = e_{jj}$ and $\Delta\epsilon_j = \Delta\epsilon_{jj}$, and the off-diagonal components are $e_4 = e_{23}$ and $\Delta\epsilon_4 = \Delta\epsilon_{23}$, etc. With this notation, $W_{mn} = W_{ijkl}$ when $n = 1, 2, 3$; and $W_{mn} = 2W_{ijkl}$ when $n = 4, 5, 6$; thus $W_{44} = 2W_{yzyz}$.