SUBMILLIMETER OPTICAL PROPERTIES OF HEXAGONAL BORON NITRIDE

A. J. Gatesman, R. H. Giles and J. Waldman
Department of Physics and Applied Physics
University of Massachusetts • Lowell
Lowell, MA 01854

ABSTRACT

The submillimeter optical properties of hot-pressed boron nitride with a hexagonal crystal structure were studied at room temperature from approximately 20 cm^{-1} to 120 cm^{-1} (500µm - 84 µm) with a Fourier Transform Spectrometer. Several grades were studied and probed both parallel and perpendicular to the material's optic axis. The material was found to behave as a negatively uniaxial birefringent crystal. In one case, the birefringence ($\Delta n = n_e - n_o$) was quite large with a value of -0.152. The material's absorption properties were also studied. For certain grades, a modest dichroism was observed. The low absorption ($\alpha < 1$ cm^{-1}) for grade A at frequencies below 38 cm^{-1} suggests the possibility for millimeter/submillimeter wave applications. Results are compared with data by other researchers on related materials.

INTRODUCTION

Boron nitride (BN) has received considerable attention within the last few years due to its favorable mechanical, electrical, optical and chemical properties over a wide range of temperatures. BN crystallizes in two forms; cubic (zinc blende) and hexagonal structures. BN films grown by processes such as CVD and sputtering have the cubic crystal structure (similar to that of GaAs). This material is used in applications such as transmitting substrates for X-ray lithography masks, high quality insulating films for metal-insulator-superconductor (MIS) structures, and coatings to increase the hardness of materials.[1] The material used in this study was hot-pressed BN where the raw material is subjected to a high uniaxial compressive force at an elevated temperature. This results in an orderly arrangement of the boron and nitrogen atoms (a structure similar to that of graphite, see Figure 1). Boron nitride has previously been studied in the ultraviolet, optical, infrared, and microwave frequencies.[2,3,4] Its low absorption coefficient in the microwave has made BN a candidate for window material for gyrotrons, free electron lasers and reentry vehicle communication systems.[4,5] This paper reports the optical properties of hexagonal BN (*h*-BN) in the submillimeter region of the spectrum.

A material with a hexagonal crystal structure is known to be optically anisotropic with a single optic axis coinciding with the axis of crystal symmetry.* In this case, the dielectric constant ε is a 3 x 3 tensor. The dielectric tensor can be shown to be symmetric[7] and the nine components reduce to six where $\varepsilon_{ij} = \varepsilon_{ji}$ for $j \neq i$. Furthermore, there exists an orientation of the cartesian coordinate system where its axes are alined with the material's preferred axes (i.e. in the hexagonal case, one of the cartesian axes alined with the optic axis). This coordinate system is referred to as the principal set of axes and the six components of ε will reduce to three (ε_x, ε_y, ε_z) where the off axis elements are zero.

*Materials with a tetragonal, trigonal or hexagonal crystal structure have a single optic axis and are said to be uniaxial. Orthorhombic, monoclinic and triclinic systems have two optic axes and are said to be biaxial. The remaining crystallographic system, cubic, is optically isotropic.[6]

With the cartesian coordinate system alined along the materials's preferred axes as in Figure 1, ε_y will equal ε_z due to the degree of symmetry inherent in the hexagonal crystal structure. In this case, the x axis is the axis of symmetry (the optic axis) and the planes of atoms are in the y-z plane. This leaves the dielectric constant (or equivalently the complex refractive index, n - ik) to be determined for just *two* cases; (1) the electric field parallel to the x axis and (2) the electric field in the y-z plane.

Hot pressed hexagonal boron nitride was obtained in four grades (A, HP, M, M26) from The Carborundum Co. in Niagara Fall, NY. Two samples per grade were provided; one whose flat surface was parallel to the crystal planes and one whose flat surface was perpendicular to the crystal planes. With a controlled incident linear state of polarization, the response of both parallel and perpendicular directions to the optic axis could be probed.

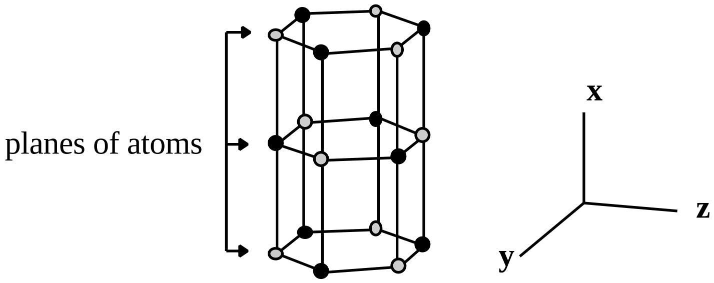

Figure 1 Orientation of the cartesian cooridinate system to coincide with the material's preferred axis and the arrangement of planes of atoms

EXPERIMENTAL

The optic axis of the parallel cut samples is obviously normal to the sample surface. For normally incident radiation, these disks were expected to behave as optically isotropic materials. The optic axis of the perpendicular cut samples lay somewhere along a diameter and had to be located. This direction was determined in the following manner. 513μm radiation from a CO_2 optically pumped submillimeter laser was propagated through a pair of wiregrid polarizers, the wires oriented orthogonally with respect to one another. The BN sample, mounted in a computer controlled rotation stage, was situated between the two wiregrids as shown in Figure 2.

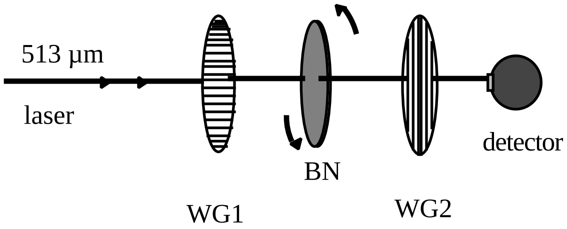

Figure 2 Experiment to determine the location of the optic axis on the perpendicular cut samples

The laser radiation, linearly polarized by WG1, was incident on the BN which was rotated while the detector collected intensity data. In general, the birefringent properties of the perpendicular cut BN depolarized the incident linear state of polarization and WG2 passed a portion of this to the detector. However, when the optic axis of the BN crystal was parallel *or* perpendicular to the wires of WG1, the linear state incident on the BN remained polarized since this state probed only ε_x or ε_y, not a combination of both. For these orientations (obviously four orientations per sample) WG2 reflected all radiation incident upon it and the intensity at the detector was zero. This procedure allowed for the determination of the two orthogonal axes in the plane of each perpendicular cut sample to within two degrees.

In order to distinguish the optic axis, a Fourier Transform Spectrometer was employed from 18 cm^{-1} to 118 cm^{-1}. Our instrument has been optimized for long wavelength data collection by using a liquid helium cooled silicon bolometer with a cooled low-pass filter as the detector. Data was collected with a resolution of 0.1 cm^{-1}. A pair of wiregrid polarizers configured with their wires parallel were positioned in front of the BN to insure a well defined linear state incident on the material. Twelve spectra were collected in total. The first four were grades A, HP, M and M26 in the parallel orientation. The remaining eight were the four grades with the optic axis parallel and perpendicular to the incident linearly polarized radiation. The transmission spectra for grades A and M26 in the perpendicular orientation are shown in Figure 3.

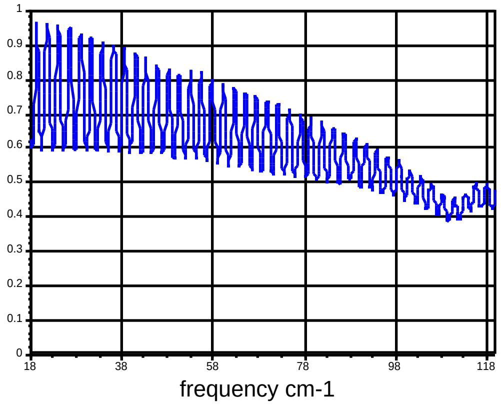

Figure 3a
Grade A   extraordinary (optic) axis

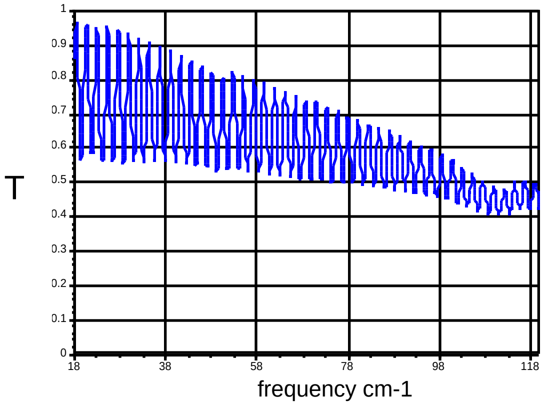

Figure 3b
Grade A   ordinary axis

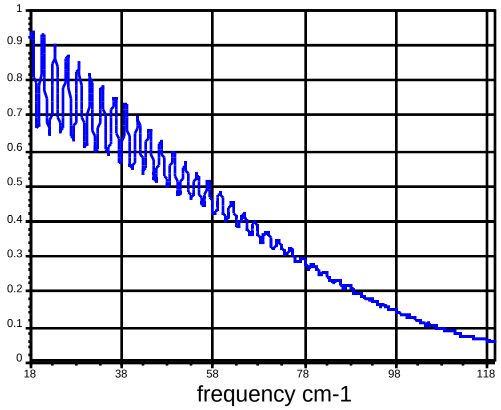

Figure 3c
Grade M26   extraordinary (optic) axis

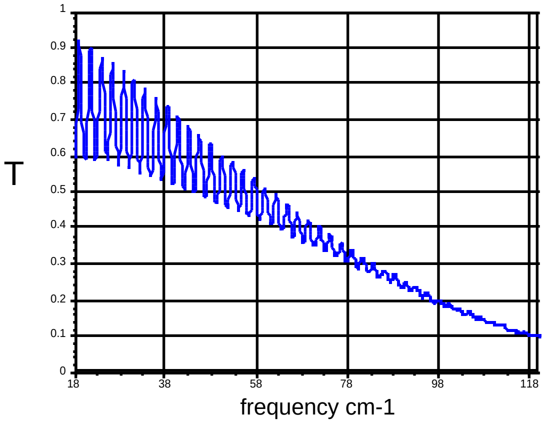

Figure 3d
Grade M26   ordinary axis

Spectra for grades HP and M in the perpendicular orientation are similar to (but not identical) to the M26 spectra and are not shown. The spectra of the parallel cut samples are not shown as they were nearly identical to one of the two perpendicular cut samples (as expected) and were useful only in determining which axis was the extraordinary (optic) axis and which one was the ordinary axis. Grade A is interesting because of its lower loss and M26 is interesting because of its dichroic behavior. Both of these points will be returned to later in the Results and Discussion section.

Derivation of the Optical Properties

The material's refractive index n, and absorption coefficient α, were both determined from the transmissivity data. Characteristic of all of the spectra is the rapid oscillation which is caused by the interference between the front and back surfaces of the sample (channel spectra). A transmission maxima occurs when an integral number of wavelengths within the material equals twice the thickness;

$$m\,\lambda_n = 2t,$$

where λ_n equals λ/n and m = 0, 1, 2, 3,... or written another way: $n = \frac{m}{2\,t\,\nu}$ where ν is the frequency in cm^{-1}. The thickness of the samples were measured with an uncertainty of ±0.0001" (±3µm). With the order number and location in frequency of each of the maxima determined, a value of n could then be associated with each peak of the spectra. Values of n for the extraordinary (optic) axis and perpendicular to it (ordinary axis) are given in Figure 4 and are labelled n_e and n_o respectively. The uncertainty in n is ± 0.006 and is due primarily to the uncertainty in the material's thickness ($\delta t/t \approx 0.003$).

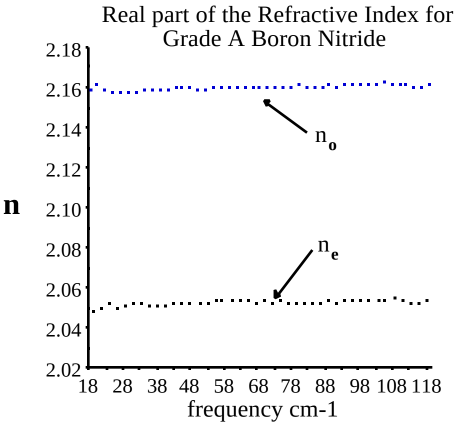

Figure 4a

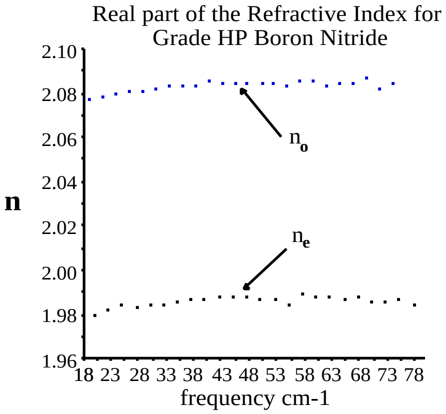

Figure 4b

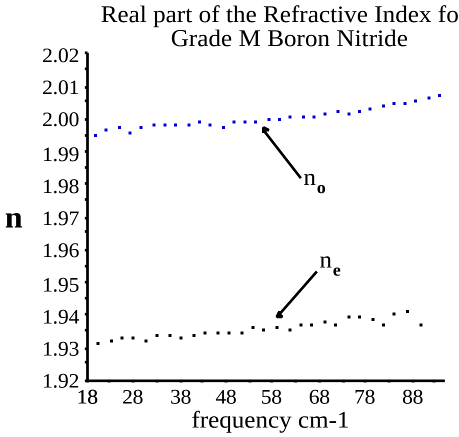

Figure 4c

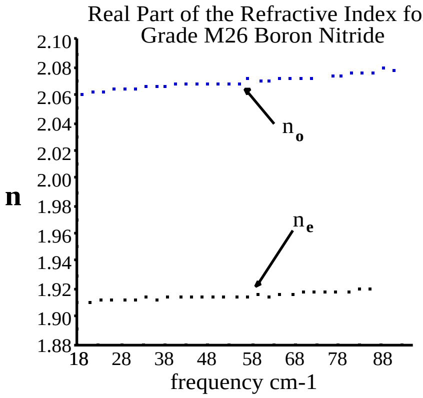

Figure 4d

Calculation of the material's absorption coefficient, α, as a function of frequency was performed in the following way. First realize that the transmissivity T through a homogeneous etalon of uniform thickness is a function of the complex refractive index, thickness and the wavelength;

$$T_{expt} = f(n, k, t, \lambda).$$

For each peak in the spectra, n, t, λ and T_{expt}. are known. This leaves the a single unknown, k, to be determined ($\alpha = 4\pi k/\lambda$). A value of k at a given peak is found by increasing k from 0 until a modelled value of the transmissivity (T_{model}) using the appropriate n, t and λ, matches the experimental value. Values of the absorption coefficient α are given for the four grades in Figure 5.

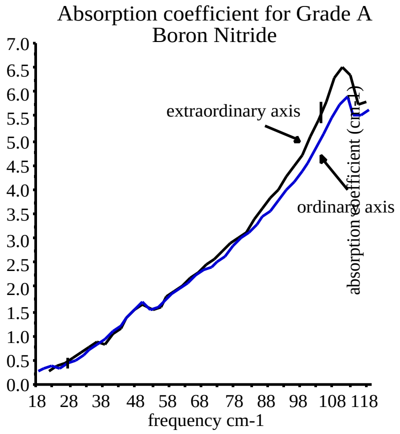

Figure 5a

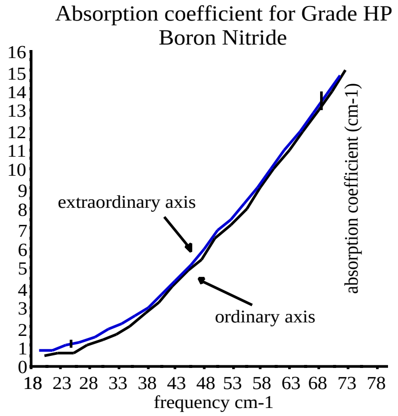

Figure 5b

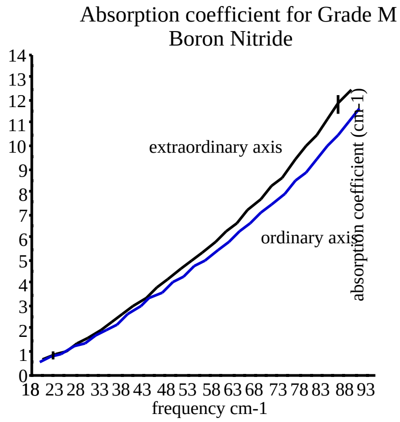

Figure 5c

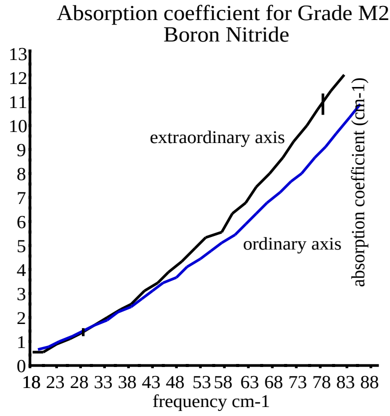

Figure 5d

The uncertainty in α is difficult to calculate because it cannot be solved analytically in terms of T_{expt}, n, λ, and t. However, since the major source of error in α is the uncertainty in T_{expt}, $\delta\alpha$ can be estimated in the following manner. The accuracy of the transmissivity data is ≤ 0.02. After a value of k is found at a particular peak that reproduces the data, it is then varied again (either higher or lower) until $|T_{model} - T_{expt}| > 0.02$. This value of k is called k_{error} and an estimate in the uncertainty in k is given by $|k - k_{error}|$. The corresponding uncertainty in α is indicated by the error bars on two data points in each of the plots. Two bars are given to indicate any slow changes in the uncertainty with frequency.

RESULTS AND DISCUSSION

The birefringence was found to be roughly constant in this frequency range for all of the grades. Values of Δn were -0.108, -0.098, -0.065, and -0.152 for grades A, HP, M and M26 respectively. Optical properties of related ceramics also show a strong birefringence. Aluminum Oxide has a rhombohedral crystal structure and is therefore a uniaxial material. Δn has been measured by Ref. 8 to be 0.36 at 100 cm^{-1}. Beryllium Oxide with a hexagonal crystal structure was found to have a birefringence[9] of 0.144 at 100 cm^{-1}. One difference between these materials and *h*-BN is that *h*-BN exhibits a negative birefringence.

All grades of BN studied were found to exhibit dichroic behavior to some degree as can be seen in Figure 5. In grades A, M, and M26, the dichroism ($\Delta\alpha = \alpha_e - \alpha_o$) is seen to be frequency dependent with increasing values towards shorter wavelengths. Grade HP is the only exception with $\Delta\alpha$ barely larger than the uncertainty at the longest wavelengths studied. In all cases the absorption measured for the electric field parallel to the optic axis was found to be greater than the absorption for the electric field perpendicular to the optic axis and so the dichroism is said to be positive.

For low loss applications in the submillimeter, grade A possesses the most desirable properties. Its refractive index remains roughly constant over the frequency range studied and it exhibits the least absorption of the four grades studied ($\alpha \approx 1$ cm^{-1} at frequencies ≤ 38 cm^{-1}).

CONCLUSION

Hexagonal Boron Nitride, a wide bandgap semiconductor, has received recent attention in the millimeter/submillimeter spectral region due to its many desirable properties. Several grades of *h*-BN were obtained from The Carborundum Company and their room temperature optical properties were studied from 18 cm^{-1} - 118 cm^{-1}. The refractive index n and absorption coefficient α were determined in the submillimeter The material was found to possess a measurable birefringence, and in some cases, exhibited a slight dichroic behavior. For low loss applications in the submillimeter, grade A appears to be the most desirable with the lowest absorption coefficient of the grades studied.

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