Hexagonal boron nitride studied by terahertz time-domain spectroscopy

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Abstract. Six different grades of hexagonal boron nitride are investigated by terahertz time-domain spectroscopy. The refractive indices and loss coefficients at terahertz frequencies are measured and are related to aspects of material fabrication and properties. Loss is shown to be due primarily to scattering. Porosity is seen to be segregated at the edges of the c-planes.

1. Introduction
Boron Nitride is a synthetic ceramic with several possible morphologies, one of which is a hexagonal form with a layered graphite-like structure, as shown in figure 1, commonly termed h-BN [1,2]. The h-BN structure consists of alternating B and N atoms in the hexagonal planes and also alternating B and N atoms along the crystallographic c-axis, forming (BN)₃ rings with very strong intra-layer bonding and weak van der Waals bonding between layers. There is a large difference in the separation of atoms in the layers (1.45 Å) and between the planes (3.33 Å) [3].

Hot-pressing methods have been developed to achieve nearly full-density shapes of h-BN, as well as BN composites with other ceramic materials. A comprehensive list of properties of h-BN is available at [2] http://www.ioffe.rssi.ru/SVA/NSM/Semicond/BN/basic.html. Although h-BN has good transparency in the far-infrared, there is little published data [1,2,4-6], and no attempt has been made to relate far-infrared transmission to aspects of material properties.

In this paper we investigate four grades of h-BN using THz time-domain spectroscopy. The variations in the refractive index and loss are discussed in relation to material fabrication and structure. The utility of h-BN as an optical material at THz frequencies is also explored.

2. Material fabrication and properties
All boron nitride specimens were manufactured by Momentive Performance Materials and are representative of commercially available forms. Table 1 lists the types of BN and their properties.

Due to the low surface energy of the c-plane, BN does not self-sinter [7]. High-density freestanding shapes are achievable by hot pressing submicron, turbostratic BN in the presence of a binder phase under temperatures approaching 2000 °C and pressures up to 2000 psi. BN/AlN composites are manufactured using similar techniques. The selection of binder phase is dictated by the final application requirements, and may be boric oxide (B₂O₃) or calcium borate (Ca₃(BO₃)₂). The binder phase may be leached from the shape after it is generated. Pyrolytic BN is manufactured by vacuum deposition from a gas phase at temperatures of 1800-1900 °C and pressures below 1 Torr.
During fabrication, the pressed plug is formed as an array of standing platelets, which assume a preferential orientation with respect to the pressing direction such that their $c$-plane is approximately parallel to the pressing axis. Each platelet consists of hexagonal crystals aligned with their $ab$-plane lying in the plane of the platelet. Materials having hexagonal crystal structure are expected to be optically anisotropic, the resulting birefringence being such that the extraordinary ray lies in the $ab$-plane and the ordinary ray is aligned with the $c$-axis (Figure 1).

Grades PBN, HBC and HBT consist of pure BN. Grades HBN and HBR contain binders, while BIN77 is a BN/AlN composite. PBN is fully dense; other grades contain varying fractions of porosity.

3. Data acquisition and analysis

The THz time-domain spectrometer (TDS) used a standard configuration incorporating a femtosecond laser, four off-axis parabolic mirrors, a biased GaAs emitter, and electro-optic detection with a ZnTe crystal and balanced photodiodes. The maximum dynamic range of the system was 5000 in amplitude, and the frequency resolution in the experiments was 7.5 GHz. The samples were placed in the collimated part of the THz beam, which had a diameter of 25 mm and was vertically polarised. Measurements were carried out in dry air in order to eliminate water absorption lines from the recorded spectra. The amplitude and phase of the THz signal as a function of frequency are obtained from the measured time-domain data of THz electric field by applying the Fourier Transform using a standard FFT application (OriginPro 8). The experimental setup and procedures are described in more detail elsewhere [8].

Loss coefficients ($\alpha$) and refractive indices ($n$) of the samples were measured by comparing THz transmission through two different thicknesses of the sample material, and were calculated from the transmitted spectra by using the equations [8]:

$$\alpha(\nu) = -\frac{2}{d_1-d_2} \ln \left[ \frac{E_2(\nu)}{E_1(\nu)} \right]$$

$$n(\nu) = 1 + \frac{c\left[ \phi_2(\nu)-\phi_1(\nu) \right]}{2\pi\nu(d_1-d_2)}$$

where $E_{1,2}(\nu)$ and $\phi_{1,2}(\nu)$ are the amplitude and phase of the THz field at the frequency $\nu$, and $d_{1,2}$ are the sample thicknesses. Loss coefficients $\alpha(\nu)$ combine contributions from absorption and scattering.

4. Results

The refractive indices and loss coefficients of the $h$-BN grades examined are summarised in Table 1. Figure 2 shows an example of data for the grades HBC. The results for HBN and HBR are similar to those in [4] (where the corresponding grades are A and HP). The THz optical properties of different BN grades may be analysed in relation to their microscopic structures.

All grades with the exception of BIN77 are birefringent with negative birefringence. The weak positive dispersion in all samples is attributed to the tail of the lowest phonon resonance at 23 THz [9].
Grade BIN77 is non-birefringent because it is isotropic on the macroscopic scale, being formed as a mixture of randomly oriented crystals of BN and AlN. The refractive index of AlN is 2.92 [10]; while the mean index of fully dense BN is 2.11 (see PBN). The refractive index of BIN77 is 2.53, and is therefore consistent with its composition of 50BN:50AlN (mol%) and 10% porosity.

Grade PBN is a fully dense, high-purity, highly oriented material, so its refractive index values lie closest to those of a single-crystal: its $n_e$ is lower than that of sintered grades, and its $n_o$ is higher, due to the more uniform and precise alignment of its crystal planes, resulting in higher birefringence.

It may be expected that the refractive indices of different BN grades will decrease linearly with increasing porosity, since less material lies in the optical path. Figure 3 depicts the relationship, where PBN is seen to lie outside the trend of other grades. The HBR grade has refractive index values below the trend, attributed to the presence of $\sim$6% of Ca$_3$(BO$_3$)$_2$ as binder. The other binder-containing grade, HBN, conforms to the trend, because B$_2$O$_3$ forms a glassy matrix with a similar refractive index to BN. The most notable feature of figure 3 is that the $n_e$ decreases with porosity, as expected, but the $n_o$ does not. This supports the view that porosity in these materials is located predominantly at the edges of the $c$-planes, and not at the low-surface-energy faces of $c$-planes. The $e$-ray is polarised in the plane of the platelets, therefore experiencing an effective refractive index which is modified (reduced) by the interstices between the platelet edges. The $o$-ray, which is polarised transversely to the platelets, should be similarly affected by interstices between platelet layers. Consequently, the fact that the $n_o$ remains constant indicates the absence of porosity between platelet faces.

Loss in ceramic materials is caused by combined contributions of absorption and scattering. Single-crystal $h$-BN has high transparency at THz frequencies [5,6], therefore losses in different BN grades, listed in table 2, are due primarily to scattering, with some contribution from binder absorption. Scattering loss is expected to rise with porosity due to the greater presence of scattering centres. As expected, loss in fully-dense PBN is much lower than in other grades. Indeed, PBN is sufficiently transparent to be a good candidate material for THz optical components. In contrast, BIN77 is much more lossy than other grades, although like BN, AlN is highly transparent [10]. The loss is attributed to increased scattering arising from the mismatch of the refractive indices of the two constituents (2.1 for BN and 2.9 for AlN). Loss in HBC, HBN and HBT indeed increases with porosity; whilst HBR has higher loss due to absorption by Ca$_3$(BO$_3$)$_2$. HBT is of interest because of its pronounced dichroism. This is attributed to porosity being segregated at the edges of the platelets, thus causing greater scattering of the beam polarised in the $ab$-plane.

![Figure 2. THz refractive indices and loss coefficient of the HBC grade of boron nitride.](image-url)
Figure 3. THz refractive indices of BN grades at 2 THz.

Table 1. Properties of different grades of Boron Nitride.

|       | PBN | HBN | HBR | HBC | HBT | BIN77 |
|-------|-----|-----|-----|-----|-----|-------|
| BN mol% | 100 | >95 | >94 | >99 | >99 | 47 |
| AlN mol% | -   | -   | -   | -   | -   | 47 |
| Binder | None | B₂O₃ | Ca₃(BO₃)₂ | None | None | Ca₃(BO₃)₂ |
| Density (g/cm³) | 2.26 | 2.10 | 2.00 | 1.95 | 1.75 | 2.43 |
| Porosity % | 0 | 7 | 11 | 13 | 22 | 10 |
| $n_e$ ± 0.002 @ 2THz | 1.915 | 2.087 | 1.995 | 2.058 | 2.015 | 2.530 |
| $n_o$ ± 0.002 @ 2THz | 2.307 | 2.197 | 2.128 | 2.200 | 2.202 | 2.530 |
| $n_e$ - $n_o$ @ 2THz | -0.392 | -0.110 | -0.133 | -0.142 | -0.187 | 0 |
| Loss ± 5% (cm⁻¹) @ 2THz | 0.85 | 2.2 | 10.6 | 3.0 | 13.1 (ε) | 70 |
|          |     |     |     |     |     | 5.2 (α) |

5. Conclusions

Six grades of ceramic BN were examined and THz optical properties were shown to be related to the material structure. Porosity was seen to be segregated at the edges of the c-planes, and loss was seen to be due to scattering. The effects of different binders and BN/AlN composite were analyzed.

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