



## $^{19}\text{F}$ and $^{11}\text{B}$ MAS NMR of Fluorinated Boron Nitride

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### Introduction

Very fast MAS  $^{19}\text{F}$  and  $^{11}\text{B}$  NMR studies of fluorinated boron nitride and related materials were undertaken on a 600 MHz spectrometer in order to probe the fluorine environments. Hexagonal boron nitride (*h*-BN, “white graphite”) is an example of a two-dimensional, insulating material of great interest because of its properties and potential uses. Fluorination will change the properties and is expected to result in a semiconductor, as has been demonstrated with fluorinated BN nanotubes.<sup>1</sup> Theoretical studies have addressed the possibility of fluorinating BN and the significance of the resulting material.<sup>2,3</sup> In general, the functionalization of two-dimensional materials is an area of intense research because of their unique properties and potential applications.

### Experimental

Very fast MAS  $^{19}\text{F}$  and  $^{11}\text{B}$  NMR studies were performed on the wide bore 600 MHz  $^1\text{H}$  frequency spectrometer (magnet #2) at NHMFL (Tallahassee).

### Results and Discussion

Preliminary  $^{19}\text{F}$  MAS studies at a lower field and with much slower spinning (4mm OD rotor) were of limited utility.<sup>4</sup> Spinning at 50 kHz (1.3mm OD rotor) at 564.6 MHz  $^{19}\text{F}$  attenuates and displaces the spinning sidebands beyond the various centerbands, thereby greatly facilitating spectral interpretation. The  $^{19}\text{F}$  studies on various materials at NHMFL demonstrated that the  $^{19}\text{F}$  signals observed when *h*-BN was fluorinated with Nafion in DMF result only from Nafion degradation products, apparently just straight chain perfluoroalkanes. In contrast, different  $^{19}\text{F}$  signals were observed with *h*-BN and cubic BN (*c*-BN) subjected to fluorination with fluorine gas. The absence of any suitable model systems with  $^{19}\text{F}$  chemical shift data severely limits our ability to interpret the dominant centerband signal at -149 ppm in fluorinated *h*-BN and fluorinated *c*-BN, but the chemical shift does appear to be reasonable for a B-F bond. The dominant and minor centerband signals cannot be from trapped fluorine gas.

Very fast spinning (40 kHz MAS) at 192.5 MHz  $^{11}\text{B}$  renders  $^{11}\text{B}$  MAS NMR studies feasible, as the second-order quadrupole-induced upfield shift is attenuated, signals from boron in asymmetric environments are significantly narrowed, and spinning sidebands are attenuated. Of particular interest is the unexpected appearance of a sharp ( $\nu_{1/2} = 324$  Hz), essentially symmetric,  $^{11}\text{B}$  centerband at -3.5 ppm (with weak spinning sidebands) in the sample of *h*-BN treated with fluorine gas. The signal suggests the presence of a symmetric tetrahedral environment (such as *c*-BN), but the transformation of any *h*-BN to *c*-BN would be totally unexpected. The half-height linewidth is barely greater than that of *c*-BN before (312 Hz) or after (309 Hz) treatment with fluorine gas, both of which give signals at -0.1 ppm. The origin of this signal in the sample of *h*-BN treated with fluorine gas is being actively investigated.

### Conclusions

Additional methodologies (UV, IR, Raman, XPS, XRD, STM, TGA) are being used to characterize fluorinated *h*-BN and *c*-BN. Preparation of a manuscript is in progress.  $^{19}\text{F}$  and  $^{11}\text{B}$  MAS NMR studies on additional related materials are anticipated in light of the very useful spectra obtained thus far.

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