



BNNT Growth in a Fluidized Bed Reactor

**Donald Lyons
HAMPTON UNIVERSITY**

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14. ABSTRACT The research activities performed under this grant represent ongoing investigations of the effectiveness of using both fluidized bed and plasma assisted nanotube synthesis for the growth of boron nitride nanotubes (BNNT). Within this context, we established new laboratories to systematically study certain key chemical pathways that are projected to determine rates and efficiencies for high yield, high quality BNNT from mixed powders of boron and lithium oxide (B + Li ₂ O). Our setups permit UV absorption and Raman spectroscopy along the vapor transport path during the growth process to investigate the presence of boron species in the reaction vapors. Experiments involving catalyst and non-catalyst systems were demonstrated for reaction temperatures below and above the melting point of lithium diborate. A chance meeting with an old colleague led us down the path of using plasma assistance to growth BNNT in a manner similar to that of researchers at the Canadian Research Council. With our combined resources, we developed a new apparatus to pursue this synthesis method. Our initial studies are encouraging enough to make the plasma-assisted nano tube synthesis (PANTS) technique the main focus of our future work.

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'BNNT Growth in a Fluidized Bed Reactor' Final Progress Report

Abstract

The research activities performed under this grant represent ongoing investigations of the effectiveness of using both fluidized bed and plasma assisted nanotube synthesis for the growth of boron nitride nanotubes (BNNT). Within this context, we established new laboratories to systematically study certain key chemical pathways that are projected to determine rates and efficiencies for high yield, high quality BNNT from mixed powders of boron and lithium oxide (B + Li₂O). Our setups permit UV absorption and Raman spectroscopy along the vapor transport path during the growth process to investigate the presence of boron species in the reaction vapors. Experiments involving catalyst and non-catalyst systems were demonstrated for reaction temperatures below and above the melting point of lithium diborate. A chance meeting with an old colleague led us down the path of using plasma assistance to growth BNNT in a manner similar to that of researchers at the Canadian Research Council. With our combined resources, we developed a new apparatus to pursue this synthesis method. Our initial studies are encouraging enough to make the plasma-assisted nano tube synthesis (PANTS) technique the main focus of our future work.

Research Objectives

The current technical approach aims to exploit the respective advantages of low- and high-energy synthesis methods for producing Boron Nitride Nanotubes (BNNT). This 'low versus high' energy designation characterizes the relative energy requirements needed to operate a given reactor design and, as a first approximation, is roughly proportional to product cost. Generally speaking, with the former (Chemical Vapor Deposition) types, relatively higher synthesis rates (50 µg/hr.) are encountered at the expense of generating particles of a wide pore radius and distribution while the latter types produce lower rates (20 µg/hr.) but a much more desirable (quality-wise) smaller pore size and distribution. Regardless of the type of reactor system employed, it is clear that surface kinetics is not the controlling factor under either operational mode. If that were the case, one would observe exponential increases in production rates with temperature and linear increases in such rates with system pressure. Neither of these outcomes is encountered in practice. Hence, the relatively modest observed increases in BNNT production rates over a substantial range of temperatures (850 °C - 3000 °C) suggest that mass transfer resistances are the rate limiting factors in such heterogeneous gas-solid systems. As a result of such observations, we are particularly interested in examining the potential role that boron (protective) oxide may play in inhibiting surface kinetics or posing a mass transfer barrier.

The goal of the present inquiry is to operate at a temperature below 1500 °C where boron oxide self-ignition is known to occur and to use selective metallic oxide catalysts as one method for moderating pore size formation and distribution. The ultimate end goal is to provide designers with engineering heuristics that can be used to scale-up BNNT production from our fluidized bed reactor and other direct synthesis systems. To accomplish this task, a high temperature furnace capable of reaching temperatures of 2000 °C is needed for preheating carrier and inlet gases entering our fluidized bed system (Figure 1 left diagram). This fluidized bed system consist of three zones: a solid preprocessing region for blending boron and oxide catalysts, an optical window region for monitoring reactor products, and an impinging jet region for preheating the reactant carrier gas (NH₃). Such beds are advantageous in that they can be operated isothermally unlike packed or fixed bed systems that can exhibit pronounced temperature gradients. The subsequent catalyst screening is conducted to determine suitable candidates systems for the larger scale fluidized bed setups. See the factorial chart in Figure 1.

Catalyst Screening Experiments Below 1500 °C

Crystalline lithium diborate is a congruent melt phase of the lithium oxide-boron oxide that melts at 917 °C. In the present catalyst screening study 99.8% pure lithium diborate containing trace impurities is used as a boron source for the synthesis of BNNT. This material, purchased from **Sigma-Aldrich**, has a nominal particle size of 60 mesh and a density of 2.44g-cm³. The unit cell is a tetragonal with dimensions of a=b=9.47 and c=10.26 angstroms. The other boron source for these experiments is a 98% boron powder of mesh size 325 that contained a somewhat higher-level of impurities. This latter material was purchased from ESPI Metals, a specialty metal powder manufacturer. The ammonia source for these reactions was the off gas generated from ammonium hydroxide decomposition at temperatures below the self-ignition temperature of ammonia (610 °C).

Two types of experiments were conducted (Figure 1) involving catalyst and non-catalyst systems performed at reactions temperature below and above the melting point of lithium diborate. The initial aim of these experiments was to demonstrate that a vapor phase is a requirement for BNNT synthesis below 1500 °C. Above this temperature, the oxide layer surrounding a boron particle burns off exposing a fresh boron surface for direct ammonia attack. An additional goal is to characterize the optical features of thermally heated lithium diborate below its melting point since the presence of new phases in the solid phase matrix can be used to monitor gas-solid kinetics.

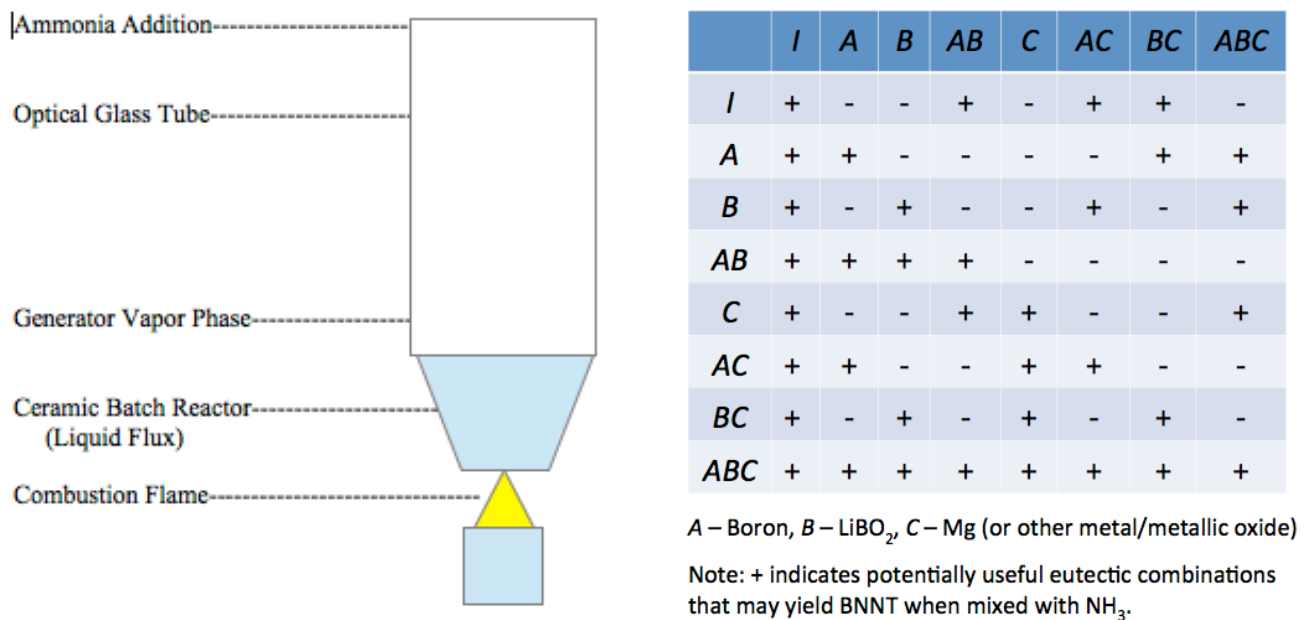


Figure 1. Catalyst Screen System and 2³ Factorial Design Matrix

Figures 2 and 3, below, contain photographs of unheated and heated lithium diborate, heated to 800 °C for thirty minutes. Note that in both pictures there is dominant single phase that contains trace impurities of boron that appear as black spots in each photograph. No fusion of individual lithium diborate particles is observed. Figure 4 is a photograph of a blend; a 50-50 mixture of lithium diborate and boron powder heated to the same temperature for thirty minutes. In this picture, fused phases are noted indicating that bonding is possible if the solids are in intimate contact since neither material has an appreciable vapor pressure at 800 °C. It is therefore reasonable to assume that the addition of boron to the lithium diborate lows the melting point of the binary mix and results in local fusing of the two species.

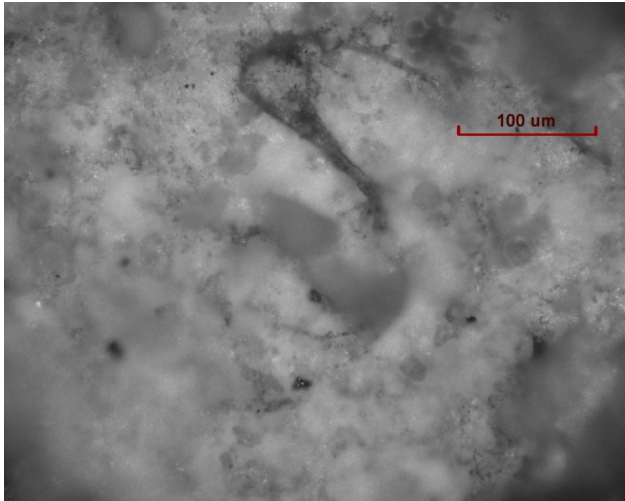


Figure 2. Unheated Lithium Diborate

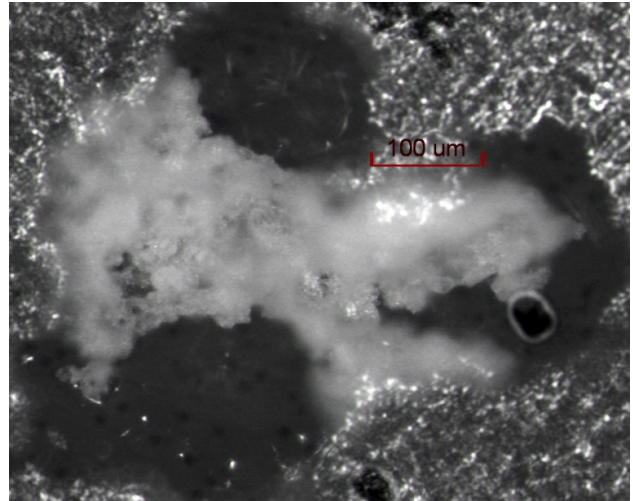


Figure 3. Heated Lithium Diborate

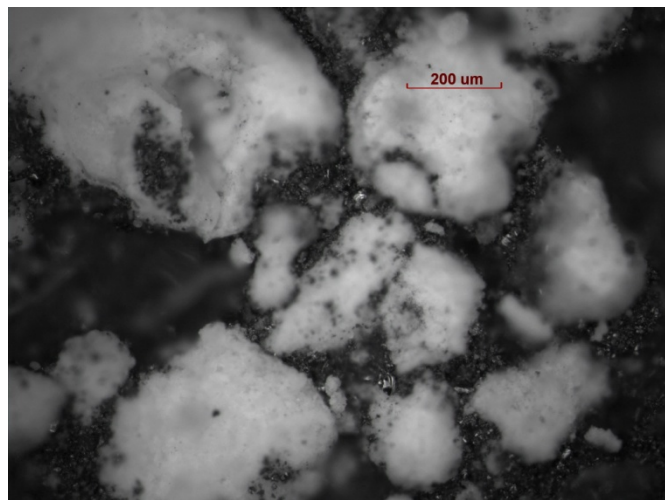


Figure 4. Fused Lithium Diborate and Boron

The pictured samples were obtained in a powdered form and were then hot-pressed in a phenolic resin for mounting samples. These mounted samples were grounded and polished in a test unit designed for handling metallurgical samples. Final polishing was carried out using a 9 μ m diamond suspension. Some of the original sample dislodged during mounting and polishing and resulted in some unevenness of the specimen surface. The dark glittering fine particles in the samples were identified as boron and the white regions as porous lithium diborate.

An uncatalyzed reaction between lithium diborate and our ammonia source was conducted at a temperature slightly above the melting point of lithium diborate. The reaction time in this experiment was less than ten minutes. We are presently in the process of determining the composition of an additional phase that has been visually observed in the reaction product. The next set of catalysis screening experiments will involve adding one of the candidate catalyst from the list in Table 1, where candidate materials were selected based upon Hume-Rothery rules and a catalyst vapor pressure/volatility metric (see Figure 5 below). We currently classify potential catalyst into five temperature groups where group 1 and 2 activate at temperatures below 1500 °C, while those in groups 3-5 are above this value. The Mg-Sn phase diagram of Figure 6 highlights the motivation for a dual catalyst system. In this diagram, note the exhibition of a low temperature eutectic at 200 °C. At this

low temperature one would expect a volatile species to be generated at a significant level. Since magnesium has been suggested as a catalyst for the lithium diborate/ammonia reaction, any material modification that enhances magnesium vapor generation is viewed as advantageous for boron nitride production.

Table 1. Group 2 Catalyst Candidate Systems

Single Catalyst	Dual Catalyst
Antimony	Magnesium/Tin
Barium	Magnesium/Copper
Calcium	Magnesium/Barium
Lead	Magnesium/Zinc
Magnesium	Aluminum/Tin

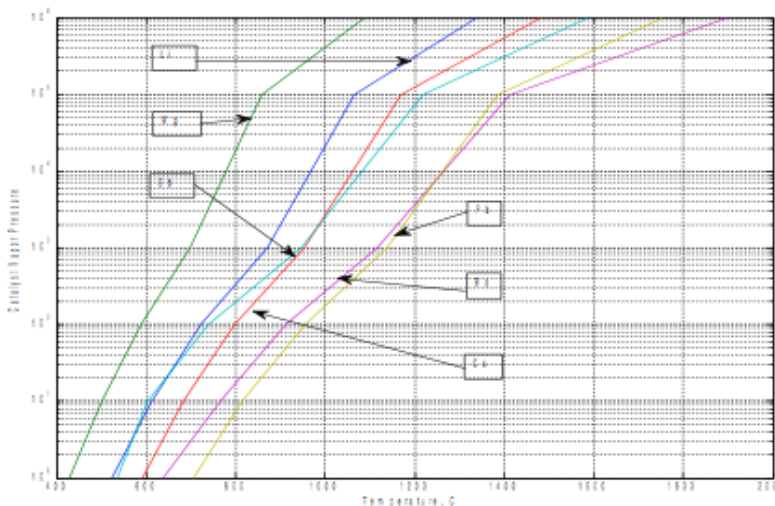


Figure 5. Catalyst Vapor Pressure Dependency with Temperature

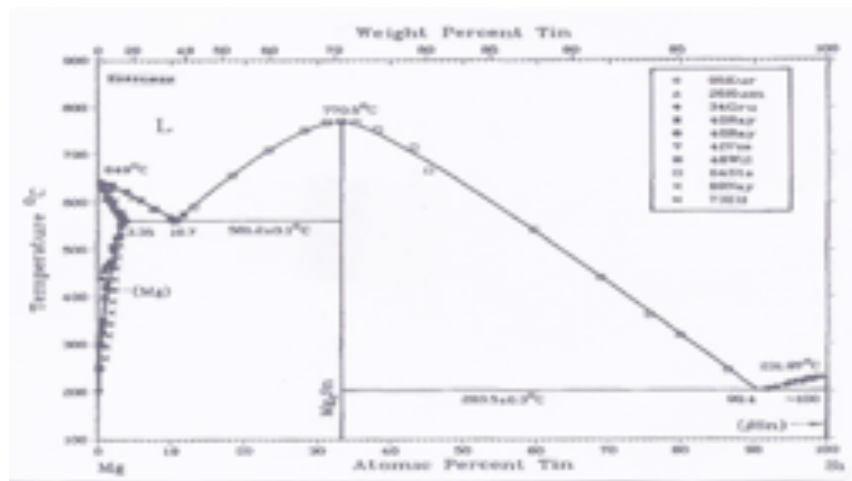


Figure 6. Magnesium-Tin Binary Phase Diagram

Optical Interrogation of Reaction Processes

For purposes of optical interrogation during the growth phase, we have designed and constructed several fluidized bed reactors to allow laser probe access. One of the reactor units is shown in Figure 7 along with a low powered probe laser where light is introduced via an optical fiber outside of the furnace and collected by a similar arrangement and employing a second optical fiber that transports the collected light to a 0.75m imaging spectrometer with an intensified CCD camera to simultaneously measure spectra over the range 190 nm to 1000 nm.

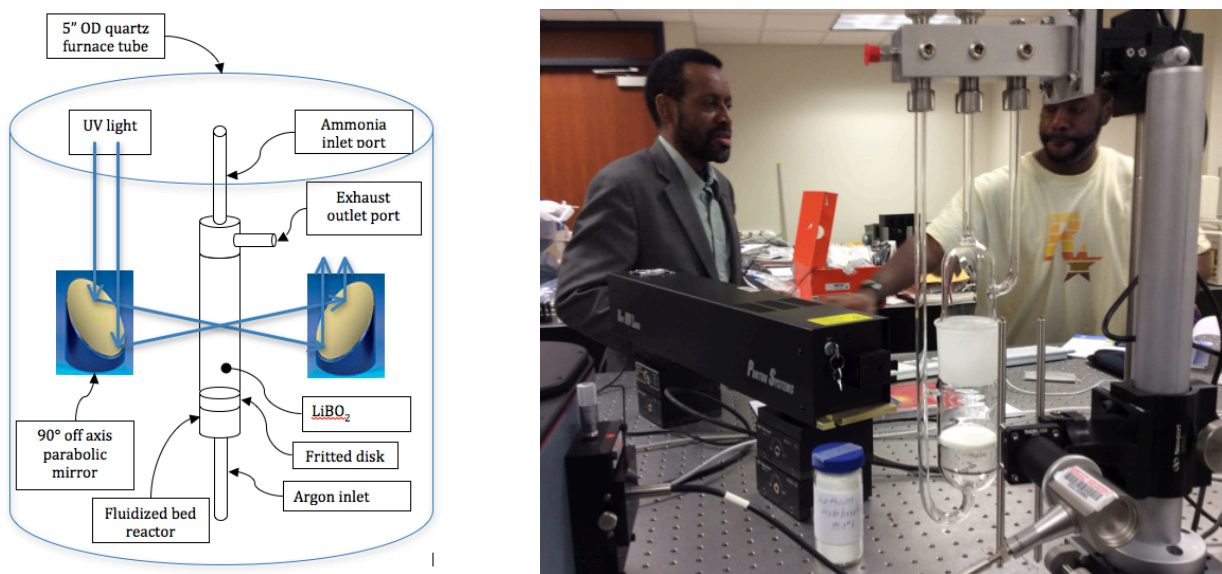


Figure 7. FBR in a vertical furnace with parabolic UV mirrors and collection apparatus

The spectroscopic technique to be used exploits the advantage of UV resonance Raman spectroscopy and its high selectivity and sensitivity for examining the vibrational spectra of materials, which have electronic absorption bands at wavelengths longer than 180 nm. The primary optical analysis of reactant-product distributions will be obtained using UV absorption and Raman spectra of vapor constituents within critical portions of the CVD reactor during BNNT formation. Deep UV resonance Raman spectroscopy will be used to investigate the chemical composition along the reactor axis. This approach provides critical insight about the reactivity of various zones in our fluidized bed reactor as well as information about the size of these respective zones. A low powered setup is used in Figure 7 with the construction of higher-powered system setups underway. An advantage is gained when the laser excitation is near a spectral resonance. The Raman cross section's frequency dependence is inversely proportional to $(\nu_e^2 - \nu_0^2)$, where ν_0 is the laser frequency and ν_e is the frequency of the transition to the excited state and thus gives large orders of magnitude enhancements over non-resonance Raman spectroscopy. Boron has strong absorption lines at 249.68 nm and 249.77 nm; close to the KrF excimer laser line at 248 nm. Raman spectral measurements at 229, 244, and 514 nm will also be made using frequency-doubled Ar-ion laser systems (shown in the background of Figure 7). In addition, this project employs a HeAg laser (224 nm) where all of the above mentioned systems are currently part of our laboratory setup. For BNNT excited by the 229 nm laser line, a Raman shift of 1365 cm^{-1} corresponding to the in-plane counter movement of B and N atoms will provide a good

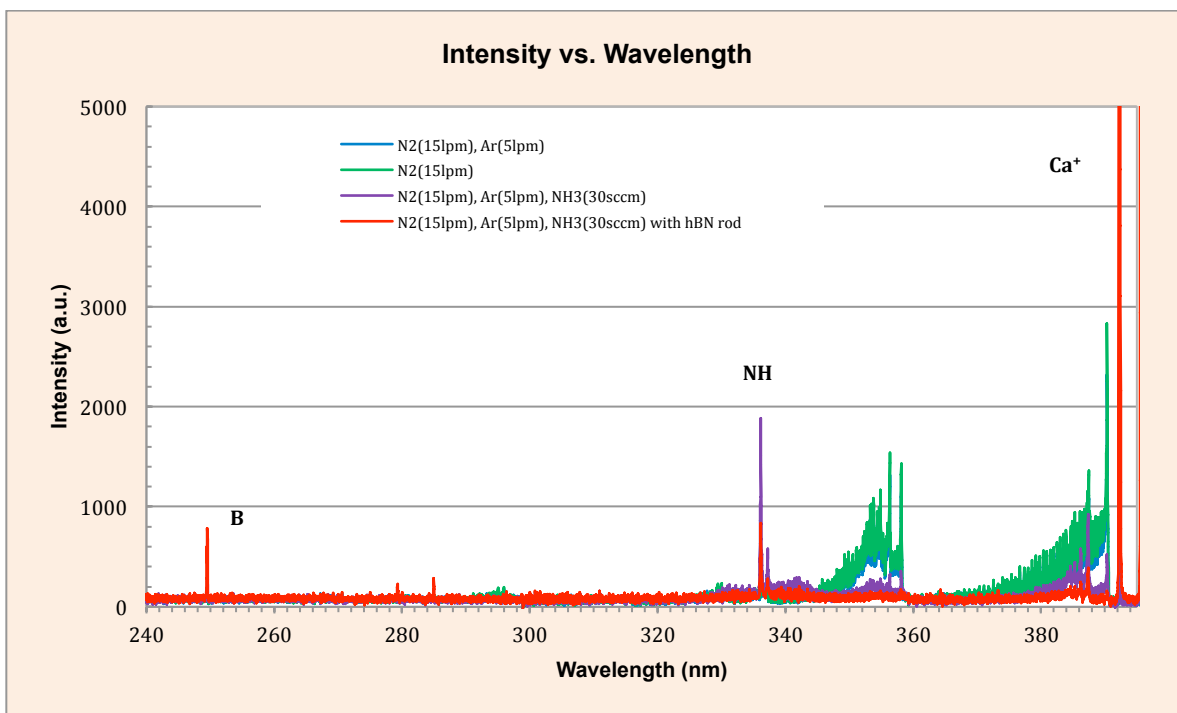
measure of material quality.

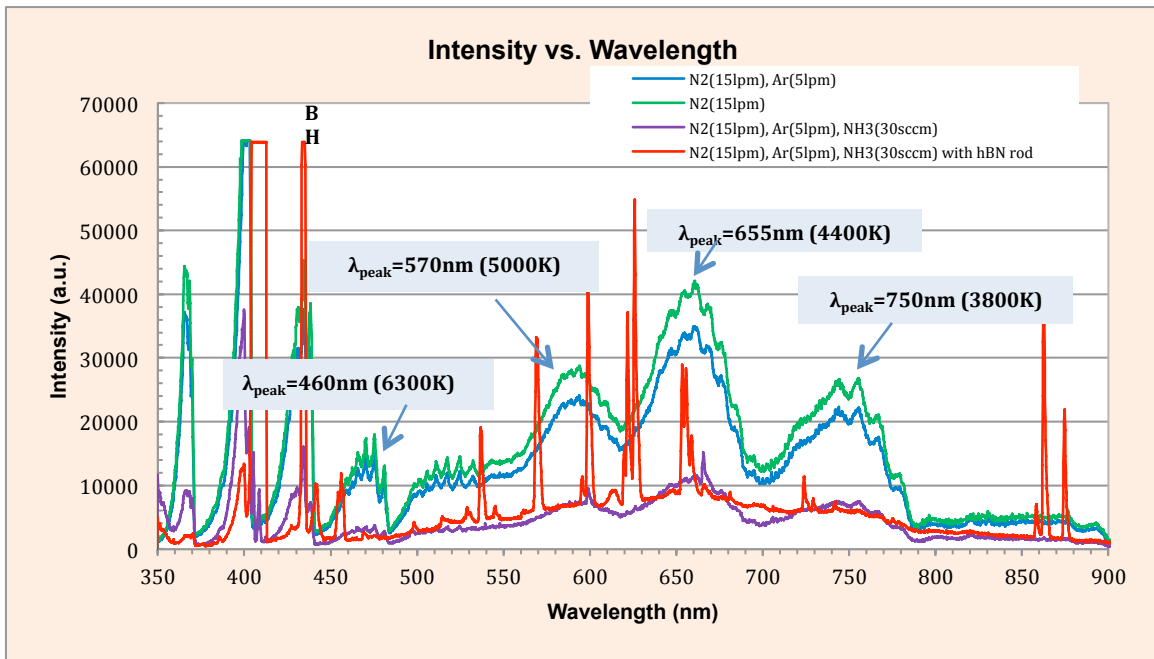
During the course of this project, a group from the Canadian Research Council (CRC) [1] developed a plasma torch method for growing BNNT at a rate of about 20 grams per hour. This far exceeds the growth rate for the best quality materials that was developed at NASA [2]. Through a fortunate meeting with a former colleague at the National Institute of Aerospace (NIA), we discovered that combining some of our existing facilities with his could result in an apparatus similar to the CRC group's, albeit with some significant differences.

We have created the apparatus and are investigating how these significant differences affect the growth of BNNT. The primary differences in our technique, which we dub Plasma Assisted Nano Tube Synthesis (PANTS), and theirs is how we generate the plasma and the precursor gas mixture we use. The CRC group uses a RF power supply operating in the MHz range and generating 60 kW power. They estimate only about 30 kW is inductively coupled into the plasma. Our system operates with two 3 kW, 2.45 GHz microwave generators and the power is coupled into the plasma with a custom designed waveguide concentrator.

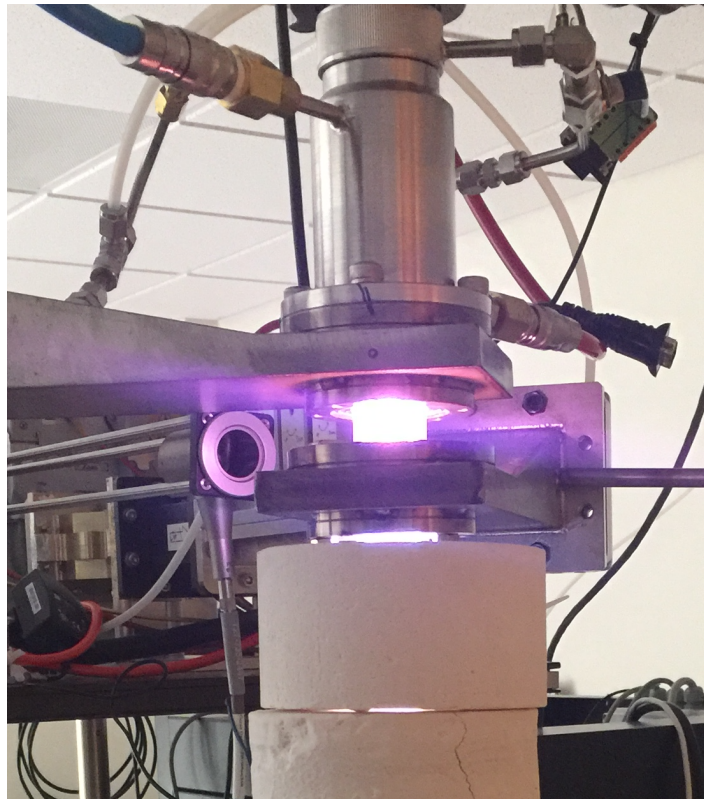
Another difference is in the precursor gas mixture. They use nitrogen, argon, and hydrogen with a combined flow rate of about 120 L/min. We replace the hydrogen with ammonia because NIA would not allow us to use hydrogen bottles in their facility, where the lab is located. Additionally, while the CRC group sifts BN powder into their plasma, we insert a BN rod of diameter 3mm – 5 mm into our plasma. On this last point, inductively coupled plasma (ICP) are hottest on their outer edge, the part closest to the RF coils, while microwave plasma is hottest at its center – making the BN rod the better route for our geometry.

To date we have learned that we can produce BNNT but that our microwave power system is not powerful enough to achieve any significant growth rate. The figure below shows some optical spectra of our plasma.





The spectral features indicate the presence of boron, NH, and BH compounds, which, according to our discussions with the CRC group are essential for the growth of BNNT. The picture below shows the plasma and the collection optics.



Brief Summary of Work

We have designed and built several experimental FBR reactors as well as establish laboratories for the production and analysis of BNNT in a new facility. In addition, we have created safety enclosures for toxic gas handling as well as nanoparticle collection. These tasks were done under the auspices of the National Institute for Aerospace within well-established guidelines. A methodical chemical engineering study involving the development of a catalyst screening system based on the Hume-Rothery Rules and the Pilling-Bedworth Ratio for stable oxide formation is still underway to allow rapid identification of reactant mixtures capable of generating high levels of the active chemical transport species and resulting in a 2^3 level experimental factorial design to identify optimal reactant mixture ratios. We also established a new collaboration with a colleague from NIA and built an experimental apparatus for plasma-assisted synthesis of BNNT. This has shown more promise than the fluidized bed research effort and will likely be the focus of our future work.

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Abstract

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