Synthesis and characterization of boron nitride microtubes

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ABSTRACT
Boron nitride microtubes (BNMTs) are successfully synthesized via a simple technique at 1200 °C. The method and logics used in the present study are relatively different and easy in comparison to previously synthesized boron nitride nanotubes, boron nitride microtubes and boron-carbon-nitride microtubes regarding the choice of precursors, experimental set up and reaction atmosphere. Field emission scanning electron microscopy (FESEM) shows a unique pipe-like morphology of the as-synthesized BNMTs with thin wall structure and larger internal space. X-ray photoelectron spectroscopy (XPS) survey shows B 1s and N 1s peaks at 191 eV and 398.7 eV that represent hexagonal boron nitride (h-BN) composition of synthesized microtubes. Raman spectroscopy demonstrates a peak at 1372.53 (cm⁻¹) that corresponds to E2g mode of h-BN.

Keywords: BNMT, Experimental Setup, Reaction Atmosphere, Growth Duration.

1. INTRODUCTION
Hexagonal boron nitride is a wide band gap semiconductor,(¹) with a direct band gap of 5.97 eV.(²) It is a normal phase of BN, stable at room temperature and pressure with a structure similar to that of graphite, but alternative boron and nitrogen atoms substituted for carbon atoms.(³)

The demand for the preparation of micro or nanosize materials with high quality is increasing due to their frequent use in the development of small size optoelectronic devices.(⁴,⁵) The synthesis of carbon nanotubes (CNTs) or boron nitride nanotubes (BNNTs) to some extent have fulfilled this demand of modern technology. BNNTs are the cylindrical structures of hexagonal boron nitride with diameter in the range of 1–100 nm and length up to several micrometers.(⁶,⁷) They were theoretically predicted in 1994,(⁸) and experimentally discovered in 1995.(⁹) The discovery of BNNTs has opened new ways for making devices with excellent properties. These properties of BNNTs are almost similar to carbon nanotubes;(¹¹) however, CNTs can be conductor or semiconductor dependent on the chirality or helicity of the tube whereas BNNTs are large band gap semiconductors with electronic properties independent of helicity or diameter.(¹²–¹⁴) Helicity independent electronic properties of BNNTs have made it an excellent choice for making (electronic) devices with uniform electronic properties.(⁴,¹²,¹³,¹⁵,¹⁶)

An almost similar relation exists between boron nitride microtubes (BNMTs) and BNNTs i.e., BNMTs have almost all the features and advantages of BNNTs.(⁴) BNMTs due to their ionic origin are large band gap semiconductor with electronic properties independent of geometry or morphology of the tube. They have nanoscale walls (10–100 nm) and larger internal space, which make a unique pipe like morphology. This pipe like morphology (of BNMTs) can efficiently be used (like carbon microtubes) as a carrier of larger size bio-molecules, and inorganic nanoparticles in micro-reactors, micro-fluids devices and targeted drug delivery systems.(¹⁷–¹⁹) BNMTs with thin...
walls, made of h-BN layers have high chemical stability, excellent mechanical properties and high thermal conductivity. Due to their reduced wall curvatures they have better crystallinity as compared to BNNTs. Further, they exhibit an intense deep Ultraviolet (UV) emission, which can be observed even at room temperature. The better crystallinity and large cross-section area for thermal neutron have made it an excellent choice as a neutron sensing element in a solid state neutron detector. The detector thus develops is predicted to have much better efficiency than any other solid state neutron detector.[20,21]

BNMTs have previously been synthesized from Li$_2$CO$_3$ and B at ~1350 °C,[19] however the experimental set up used is not only a bit complex but also relatively expensive. Furthermore, due to induction heating the size and morphology of the final product is very difficult to control at a desired location.[22] Therefore a relative simple experimental set up has been designed and used for the control synthesis of BNMTs.[22,23] This experimental setup is further simplified with a few simple modifications and is successfully used for the synthesis of BNMTs at a relative low temperature of 1200 °C (as compare to 1350 °C,[19]). In order to avoid any other complication, same type and precursor’s ratio are used for the current synthesis of BNMTs.[22] But, for the hope of better results, the as used precursors were selected in nanoscale dimension. The full details are mentioned in the following sections.

2. EXPERIMENTAL DETAILS

An extremely simple technique is used to synthesize boron nitride microtubes at 1200 °C. B, MgO and γ-Fe$_2$O$_3$ of 99.9% purity are used as a precursor. By the intention of getting some improvement in the final results, some modifications have been made in the experimental setup, quantity and size of the previously used precursors and internal environment.[22] Experimental setup is used without vacuum or evacuation. Instead of vacuum, NH$_3$ gas is used as a reaction atmosphere inside the chamber.

A total of 400 mg of precursors in the form of nanoscale amorphous powder were used during the experiment for the synthesis of BNMTs. All these precursors were mixed in 2:1:1 ratio inside an alumina boat. The boat is covered with a few Si-substrates and placed inside one end closed quartz tube near the closed end. The tube is then inserted into the quartz tube chamber of the furnace in such a way that the open end of the inner quartz tube is toward the gas inlet. The furnace is then sealed closed and turned on to heat up the precursors up to 1200 °C in the presence of NH$_3$ gas flow at a rate of 200 sccm. At 1200 °C, the system is kept in such a condition for one hour. After 1-hour the system is allowed to cool down to room temperature.

At room temperature, white color BNMTs are found deposited on Si substrate and on the inner walls of alumina boat, as shown in Figure 1. The synthesized sample is then characterized with the help of Variable Pressure Scanning Electron Microscope (VP-FESEM or FESEM, Model: Zeiss Supra 55 VP), Raman Spectroscopy (Model: Horiba Jobin Yvon HR800) and X-ray Photon Spectroscopy (XPS, Model: Thermo Scientific K-Alpha). The details are given in the following section.

3. RESULTS

Unlike previously reported BNMTs,[4,24] a bit different mechanism based on the idea behind previously synthesized vertically aligned CNTs,[25] is effectively used for the synthesis of BNMTs in the present study. Both MgO and Fe$_2$O$_3$ are selected as precursors with B, because they are effective producer of B$_2$O$_2$ and catalysts.[26] During the experimental run, the precursors are heated up to 1200 °C. During this stage, MgO and Fe$_2$O$_3$ react with B to produce B$_2$O$_2$, Fe and Mg particles. Subsequently the as produced Fe and Mg particles make Mg–Fe alloys and deposited at the top of Si-substrate. The flow of ammonia etch away Mg particle from the deposited Mg–Fe alloys on Si-substrate and thus produces nucleation sites in Fe particles (remained deposited) on Si-substrate. At higher temperature NH$_3$ decomposes into nitrogen and hydrogen. Nitrogen reacts with B$_2$O$_2$ and produces BN species. These BN species diffuses into the nucleation sites on Si-substrate. When their partial vapor pressure is sufficient enough, they grow in the form of microtubes following the nucleation sites as pattern.

The FESEM analysis of the size and morphology of the synthesized sample is shown in Figures 2 and 3. Figure 2 shows a low magnification FESEM image of the synthesized BNMTs on Si-substrate. The tubular morphology of the synthesized BNMTs can clearly be seen in the as shown micrograph. Such a unique tubular morphology of the BNMTs with FESEM result has rarely been reported by other researcher in the past.[24] Normally TEM is used to analyze the tubular morphology in such cases,[4] however, in the present work the tubular structure of the synthesized sample is shown with the help of FESEM.

From the top view, two kinds of morphologies can be seen in the synthesized sample. First, clear view of the
of 651.05 nm of the BNMTs synthesized in the present study.

Figure 3 is the higher magnification FESEM image of the same sample, showing a clear view of the tubular morphology of the BNMTs. Here again, the diameters of the tubes are calculated with the help of FESEM measuring tools, as shown in the inset images of Figure 3. The tubes are found to have and average diameter of 604.01 nm, which is smaller than the average diameter of the BNMTs shown in Figure 2. It means that the BNMTs in the present sample are not uniform in diameter and wall thickness. The diameter vary from tube to tube in the range of 580–690 nm (with an overall average of 627.52 nm) whereas the wall thickness from 10–100 nm. The button mushroom like morphologies lying around these tubes are assumed to have either cut off from the top of these tubes or still stick to their original position. At higher magnification, the top of these species and the spaces or empty locations are still found to have crakes and apparently look like to be covered with a black and white wool carpet. It has also been observed in Figure 2 that the diameter of the lower part of the tube is relatively small as compared to the upper part of the tube. It might be due to the presence of ball like or button mushroom like morphology which is assumed to have cut off from the tube later on.

The elemental compositions of the synthesized BNMTs were analyzed with the help of X-ray Photon Spectroscopy (XPS) with an X-ray source of Al K Alpha. The full range XPS survey thus obtained is shown in Figure 4. The survey shows several peaks at binding energies of 190.8, 398.5 and 533.18 eV. The B 1s peak centered at 190.8 eV (inset: upper left of Fig. 4) and N 1s at 398.5 eV (inset: upper right of Fig. 4) correspond to h-BN according to available literature. The O 1s peak at 533.18 eV may either be due to the as-used Si substrate or formation of B2O3 in the sample, which might be the secondary species or by-product observed in the FESEM micrographs shown in Figures 2 and 3.

The synthesized sample of BNMTs is also characterized together with the Raman spectroscopy to confirm its constituents and phase. The Raman spectrum is shown in the Figure 5. The major peak at 1372.53 (cm⁻¹) reported here, corresponds to the \(E_g\) mode of h-BN reported here, with a Full Width and Half Maxima (FWHM) of \(\sim 19\) (cm⁻¹). This result is a bit broader as compared to the one reported for the bulk h-BN. This broadening of the peak is a sign of small micro-size crystallites of h-BN. A smaller peak has also been observed at 1122.15 (cm⁻¹) that correspond to \(H_2BO_3\), which might have formed by the interaction of laser with moisture in the air and B2O3 in the sample. Figure 2 images the FESEM; there were some undeveloped or powder like morphologies in between the microtubes, which can rightly be assigned to the presence of B2O3 (which has already been verified by the XPS analysis) that later on leads to the formation of \(H_2BO_3\) during the Raman spectroscopy of the sample.

**Fig. 2.** Low magnification FESEM micrograph shows a clear tubular view of the synthesized BNMTs on Si-substrate at 1200 °C. The inset images on the upper left hand corner and bottom right hand corner show the calculated diameter of the BNMTs with help of FESEM measuring tools.

**Fig. 3.** High magnification FESEM micrograph shows a unique pipe like morphology of the synthesized BNMTs on Si-substrate at 1200 °C. The inset images show the calculated diameter of the BNMTs with help of FESEM measuring tools.
for the synthesis of BNMTs and B-C-NMTs. Second, the experimental setup used is self-modified, extremely simple without any vacuum or inert gases. This kind of the experimental setup is a bit different from the one used for synthesis of BNNTs, or BNMTs. Third, the use of NH₃ gas as a reaction atmosphere.

Changes in the experimental parameters are the possible reason for current morphology and diameter of the synthesized BNMTs. The main experimental parameters which can cause a change in quality, quantity, size and morphology of any nanostructure material are precursor’s type, ratio, experimental setup, reaction atmosphere, final temperature and growth duration etc. A change in any of the above parameters will result in a change in the diameter of any as produced final product. Such a change in diameter with respect to experimental parameters has been observed during the synthesis of BNNTs, BNMTs and B–C–N ternary microtubes. The analysis of such a change has been summarized in Table I.

According to the comparative analysis shown in Table I, only the development of a single precursor (Li₂O or Li₂CO₃) and an increased growth duration (3-h instead of 2-h) makes a huge difference in the diameter of synthesized BN products. However, in either of these works, no apparent role of growth duration at final temperature has been discussed to be responsible for such a huge change in the diameter of the final product. Since no role of Carbon from Li₂CO₃ has been stated in the formation mechanism for BNMTs, therefore, in the light of their further work, it is strongly believed that only the growth duration was responsible for their results (BNMTs). Also in the light of our experimental work, it is believed that the same results for BNMTs can easily be reproduced by using B and Li₂O (instead of B and Li₂CO₃) as precursors in a reduced growth duration but with similar experimenters’ parameters. Furthermore, synthesis of B–C–N ternary microtubes have been reported at 1200 °C by using similar precursor and experimental conditions, except BN-crucible, which was replaced with graphite crucible. Carbon for the formation of B–C–N is claimed to be supplied by CO/CO₂ formed through the oxidation of graphite crucible. It is also a fact that the majority of the graphite crucible is designed in such a way that it can easily withstand with a temperature above 1200 °C. Further it has mentioned that Carbon from Li₂CO₃ decomposition was available at lower temperature. Therefore, it is assumed that lower temperature (1200 °C) is responsible for utilizing C from Li₂CO₃ for the formation of B–C–N microtubes instead of CO/CO₂ due to oxidation of graphite crucible. It has also been stated that the precursors were used in 1:1 ratio, so if C is claimed to be included due to oxidation of graphite crucible then it would have highly affected the as used ratio of the precursor and the final product would have been some other compounds with a lot of carbon-containing impurities.

## 4. DISCUSSION

Though BNMTs synthesis with a bit larger diameter and length have been reported previously, however, the present work is unique with respect to a few aspects. First, the precursors type and ratio used is the same as in the synthesis of BNNTs, but different from those used in the present study. The B 1s peak centered at 190.8 eV (inset: upper left) and N 1s peak at 398.5 eV (inset: upper right) correspond to h-BN (BNMTs).

### Fig. 4
Full range XPS survey of Boron nitride microtubes synthesized in the present study. The B 1s peak centered at 190.8 eV (inset: upper left) and N 1s peak at 398.5 eV (inset: upper right) correspond to h-BN (BNMTs).

### Fig. 5
Raman spectrum of the BNMTs sample synthesized at 1200 °C shows a high intensity peak at 1372.53 (cm⁻¹) that corresponds to $E_{2g}$ mode of h-BN.
In the present work, a bit different logic has been used and applied. Instead of changing the precursor’s type, their ratio or growth duration, change in the diameter of the final product was sought on the basis of modification in previously used experimental set up and reaction atmosphere inside the chamber. Unlike the previous Experimental set up, the open end of the inner test tube, was turned toward the gas inlet. Further, it has been used without any vacuum or inert gases. Instead of vacuum or inert gases, NH₃ gas was used as a reaction atmosphere inside the chamber. Thus the present work not only gives us BNMTs but also a few more logics; First, the precursor types and ratios used for the synthesis of BNNTs, can also be used for BNMTs synthesis (as in this work) with a simple modification in an experimental set up and its internal environment. Second, the same precursor type, ratio and experimental set up but with Ar gas flow as an internal environment can be used for synthesis of BNNTs. Third, further modification in the Experimental set up with the same precursors type and their ratio and Ar gas (as an alternative for vacuum) can be used for the synthesis of other BN nanostructures like Boron nitride nanowires and nanosheet etc.

5. CONCLUSION

The successful synthesis of BNMTs in the present and its analysis with previously synthesized BNMTs, BNNTs, and B–C–NMTs, showed that the synthesis of these materials not only depends on the experimental setup, precursor types and their ratios but also on growth duration and internal environment inside the experimental set up during the experiment. Elongation of the growth duration resulted in the synthesis of BNNTs, instead of BNMTs in the past whereas the change of internal atmosphere with ammonia gas flow, instead of inert gases or vacuum, resulted in BNMTs in the present work. The synthesized BNMTs are found to be of high importance as a neutron sensing element in a solid state neutron detector, neutron capture therapy, micro-fluids devices and targeted drug delivery etc.

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References and Notes

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Table I. A comparative analysis of Experimental parameters and their effects on the diameter of the final product.

<table>
<thead>
<tr>
<th>S. no</th>
<th>Precursors</th>
<th>Ratio</th>
<th>Experimental setup</th>
<th>Final Diameter (of final material)</th>
<th>References</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Vertical induction furnace</td>
<td>Horizontal tube furnace</td>
<td></td>
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<tr>
<td>1</td>
<td>B, Li₂CO₃</td>
<td>1:1 (in BN-Crucible)</td>
<td>Vacuum: ~2 × 10⁻¹ Torr 1100–1350 2-h</td>
<td>x x x</td>
<td>1–3 μm (BNMTs) [4]</td>
</tr>
<tr>
<td>2</td>
<td>B, Li₂O</td>
<td>1:1 (in BN-Crucible)</td>
<td>Vacuum: ~2 × 10⁻¹ Torr 1100–1350 3-h</td>
<td>x x x</td>
<td>Sub–10 nm (BNNTs) [35]</td>
</tr>
<tr>
<td>3</td>
<td>B, Li₂CO₃</td>
<td>1:1 (in graphite Crucible)</td>
<td>Vacuum: ~1200 2-h</td>
<td>x x x</td>
<td>1–5 μm (BCNMTs) [17]</td>
</tr>
<tr>
<td>4</td>
<td>B, Fe₂O₃, MgO</td>
<td>2:1:1 (in Al₂O₃ boat)</td>
<td>x x x</td>
<td>Vacuum: ~30 mTorr 1200 1-h</td>
<td>10–100 nm (BNNTs) [22]</td>
</tr>
<tr>
<td>5</td>
<td>B, Fe₂O₃, MgO</td>
<td>2:1:1 (in Al₂O₃ boat)</td>
<td>x x x</td>
<td>NH₃ gas 1200 1-h</td>
<td>580–690 nm (BNMTs) Present work</td>
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