

# The effect of milling parameters on synthesis of high yield boron nitride nanotube

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In this study, high-yield Boron Nitride Nanotubes (BNNT) were synthesized by using the high energy ball milling method. Hexagonal Boron Nitride (h-BN) powder was used as starting powder and the powders were subjected to milling process for different milling rotations and different milling periods in a planetary ball mill (Fritsch Pulverisette 7 Premium Line). The powders obtained after providing the milling process, were annealed inside a tube furnace under  $\text{NH}_3+\text{Ar}$  atmosphere at  $1300^\circ\text{C}$  for a period of 2 hours. In conclusion, BNNT's were produced by using this technique. The tubes produced have been examined by use of X-ray diffraction analysis (XRD), high resolution transmission electron microscopy (HR-TEM).

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*Keywords:* Boron nitride, Nanotube, Milling, High energy ball mill

## 1. Introduction

After the Carbon Nanotube (CNT) was discovered in 1991, scientists have started to investigate other materials which have the same tube structure [1]. Boron Nitride Nanotubes (BNNT) is one of these materials. Theoretically, BNNT was discovered by Rubio in 1994 and was successfully synthesized by Chopra in Berkeley University in 1995 [2,3]. BNNTs are a new alternative of CNTs which have been frequently used in different fields recently. Various techniques have been developed in order to produce high amounts of BNNT. However, their being expensive prevents the large scale production thereof [4]. Also the fact that these produced tubes cannot be obtained in standard quality and dimension makes them insufficient in meeting the requirements of industry and researches. Another one of the methods used for producing BNNT is milling and annealing method [5]. This method enables the material production in short periods with the lowest investment and production costs [6]. Milling and annealing method has two stages; and at the first stage, milling occurs at room temperature. In the next stage, materials are annealed at a relatively low temperature [7]. In these two processes, creation of core and dispersion occur by means of milling, and enlarging from these cores takes place in annealing. In summary, B and N clusters to be used as a free atom source at atomic scale, which is obtained as a result of milling, have been used for enlargement of the nanotubes by subjecting to heat treatment at low temperatures with the addition of catalyst powders [8].

This study investigated effect of milling rotation and milling time on BNNT product amount grinded in high energy ball mill in different rotations and then annealed using starting h-BN.

## 2. Experimental procedures

Milling experiments were performed in a planetary ball mill (Fritsch Pulverisette 7 Premium Line) running at room temperature. The vials used was made of hardened steel material. As starting material, Hexagonal Boron Nitride (h-BN) powder, which was provided from Merck KGAA and has a purity level of 99 % and a starting particle size of 1-2  $\mu\text{m}$ , was loaded into vials. In the experiments, ball to powder weight ratio (BPR) 32/1 was selected. The balls used were manufactured from hardened steel material and 8 mm in diameter were used in experiments. In order to prevent powder oxidation, nitrogen gas was used as milling atmosphere. At the beginning of the experiment, milling cells were purged with nitrogen gas to be used a few times during the period of experiment. The gas was filled in the milling cell with an initial pressure of 200 kPa.

Experiments were performed using different milling rotations both in order to both examine the effect of milling rotation on nanotube and save time and energy. In consideration of the milling type that we use, milling rotation was selected as 450 and 850 rpm. Milling process was performed for periods of 4, 5, 6, and 7 hours in order to determine the ideal milling time by using different milling rotations. Iron powder (Merck KGAA, particle size  $150\mu\text{m}$ ) were milled by high energy ball milling for 3h to decrease the particle size. Nano-sized Fe powder was added as a catalytic at a rate of at.2% to the grinded starting material at the last stage of the milling process. After the milling process, powders were annealed inside a tube furnace at  $1300^\circ\text{C}$  for 2 hours under  $\text{NH}_3+\text{Ar}$  atmosphere. While the flow rate of the  $\text{NH}_3$  gas was determined as 500 ml/min, the flow rate of Ar gas was selected as 300 ml/min. At the end of annealing, it was determined that high amount of BNNTs formed. Milled and annealed samples were examined

using high-resolution transmission electron microscopy (JEOL JEM 2100F HR-TEM) and by means of CuK $\alpha$  radiation in the Bruker D9 branded X-ray diffraction analysis.

### 3. Results and Discussion

The objective of the milling process is to form the nucleus areas suitable for the subsequent annealing process and to provide the powders with mechanical energy which is the driving force for formation of the recrystallisation throughout annealing process [9]. This is because, prior to milling, hBN powders are considerably stable. Milling and amorphisation process will cause temperature of the subsequent heat treatment to considerably decrease. During this process; particle sizes of the powders would decrease whereas the surface areas would increase.

When the results of the XRD analysis of h-BN sample are examined, Figure 1.a illustrates two weak peaks [10] seen at the end of 7-hour milling process. These peaks were obtained as a result of partial

amorphisation (turbostratic structure) of the peaks at  $26.7^\circ$  (002) and  $41^\circ$ (100),  $43.8^\circ$  (101) which is the characteristic peak of h-BN. Comparing these peaks with those in non-milled powders; they started to enlarge at the end of 4-hour milling and became considerably amorphous at the end of 7 hours. During the milling process, the Fe particles which mixed into the structure with the abrasion of milling case and balls entered into reaction with the boron and formed the FeB as the milling time increased [11]. Figure 1.a illustrates that approximately  $45^\circ$  Fe+FeB peak formed at the end of 6-hour milling and, and slightly increased its intensity at the end of 7-hour milling time.

When the characteristic BN peaks of sample, which was milled for 4 hours, at  $26.7^\circ$  (002) and  $41^\circ$  (100),  $43.8^\circ$  (101) is compared with the unmilled (before milling) status; Figure 1.b illustrates a the decrease of 50 times in the intensities of the peaks. At the end of 7-hour milling, almost a full amorphisation occurred. Milling contaminations (Fe+FeB peaks), which occur at  $45^\circ$  with the intensity of the milling, were seen in each milling time.

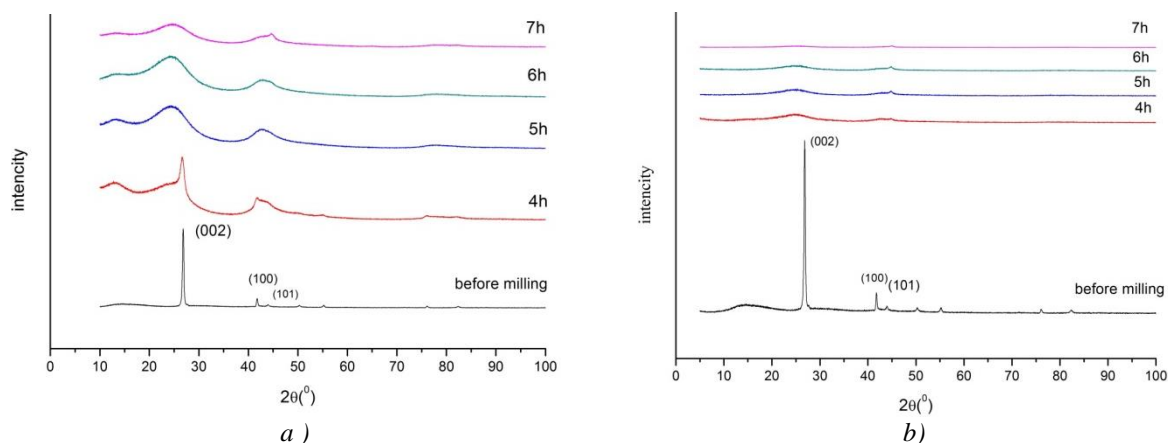


Fig. 1. XRD results of the samples with h-BN milled under  $N_2$  atmosphere for 4h, 5h, 6h, 7h, at a) 450 rpm b) 850 rpm

While the use of 850 rpm causes to increase substantially the amount of energy acquired by the powder in terms of milling efficiency and to decrease the milling time, a highly increase in the milling contaminations will ensure the formation of Boron Nitride Nanotube which could not be taken under control, even if in a small quantity in the structure. For that reason, it is considered that reaching higher milling rotations would make the amount of contamination mixing in the powders more uncontrolled. Fig. 2 illustrates the TEM image of the BNNTs been obtained due to milling contaminations. As is seen from the figure, highly thick tubes formed. The reason for this is the random size of the particles mixing into the structure during the milling process and the occurrence of tube enlargement through pretty great particles which are in proper nucleation area.

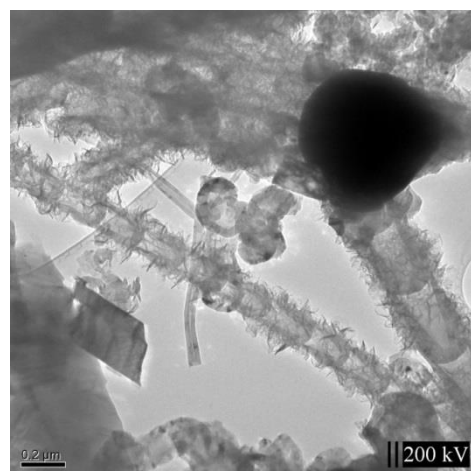


Fig. 2 TEM image of sample with h-BN milled for 7 hours under  $N_2$  atmosphere at 850 rpm and annealed under  $NH_3+Ar$  atmosphere at  $1300^\circ C$ .

In order to decrease temperature of the heat treatment, it is required to provide a considerable amount of amorphisation in the powders and to decrease the powders to nano size [6,8]. To this end, determination of the crystalline size would clarify the selection of milling rotation. The crystalline size is calculated by well known Debye-Scherrer equation formula;

$$L = \frac{0,9\lambda}{B.Cos\theta} \quad (I)$$

L: crystalline size (nm),  $\lambda$ : Wavelength (Cu  $K_{\alpha}$ = 1.5409), B: Peak intensity semi-width value (FWHM (Full Width Half Maximum),)  $\theta$ : Diffraction angle (Degree)

In milling process, balls perform free fall movement with the centrifugal impact of the mill and apply impulse forces on the powders. Powders are left both within the balls and between the cell and ball and they are severely grinded [9]. Fig. 3.a illustrates chart of the milling time - crystalline size calculated by using Equation I for the h-BN powders, grinded at 450 rpm. According to this chart, the crystal size decreased to 115 nm at the end of 4-hour milling and only below 100 nm at the end of 7 hours. As is seen in the chart, the size did not decrease to

desired level. This situation is in accordance with the results of the XRD analysis obtained at the end of milling. Using 450 rpm for the milling rotation possibly enables to decrease to the proper crystalline size with an effective milling intensity in longer periods. However this situation is not economic and practical in terms of Nanotube production since while the problem continues for obtaining the nanotube products on the basis of kg, extending the milling periods is not a good choice.

Fig. 3.b shows the crystalline size -milling time chart for 850 rpm. In the chart, at the end of 4-hour milling, the crystalline size of the powder decreased below 30 nm and was less than 20 nm at the end of 7 hours. Based on these results, at the end of 7 hour milling and at 850 rpm, we attain the necessary size decrease for the subsequent annealing process and obtain the desired disorderly structured BN. In the light of these results, increasing up to 850 rpm increased the deformation rate in the h-BN powders. Increasing the deformation rate in the powders accelerates the transmission into amorphous structure, and as a result of this the milling periods of the powders decrease .

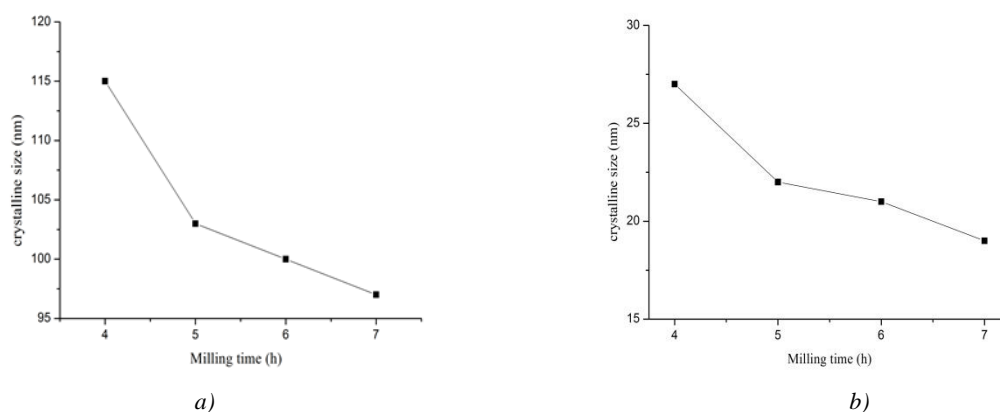


Fig. 3. Milling time-crystalline size change of the samples with h-BN at a) 450 rpm b) 850 rpm.

The energy loaded on the powders through the balls increased the internal energy and number of broken bonds of the powders. These powders need energy in order to minimise their internal energies and to transit into steady state by converting the broken bonds, in the structure, into new bonds. This energy is gained by the powders by means of heat treatment. In other words, the amount of the internal energy gained by powder through milling process directly influences the annealing temperature, the annealing time and re-crystallisation amount for annealing process, which is the second stage.

Fe powder as catalyst was added in the milled powders, and the powders were subjected to annealing process which is the next stage. Fig. 4 illustrates XRD graph of BNNTs obtained by using different milling rotations of 450 rpm and 850 rpm. As is seen from the graph, the characteristic peak (002) of h-BN, which is related with BNNT which has been obtained at 850 rpm, at  $26.7^\circ$  is significantly higher than the one obtained at 450 rpm. Based on these results, even if nanotube

products are obtained at both milling rotations, in this situation where other milling conditions are constant, changing only the milling rotation causes a pretty much variation in the amount of nanotube product [7,20].

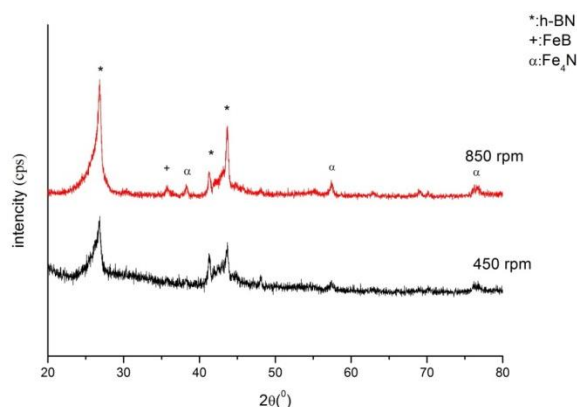
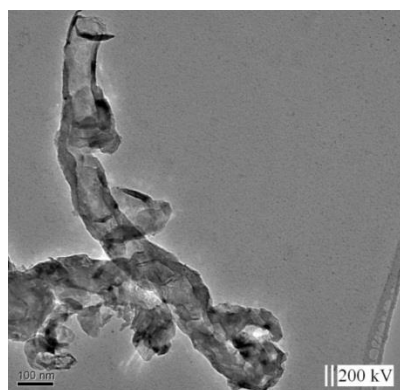
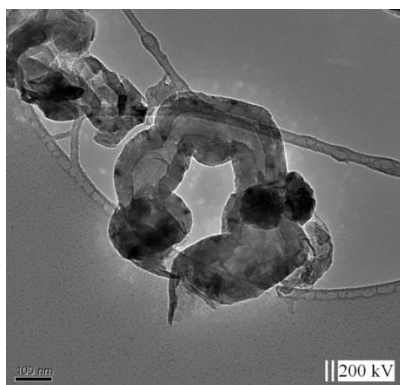


Fig. 4. XRD analysis of sample with h-BN annealed at  $1300^\circ\text{C}$  under  $\text{NH}_3+\text{Ar}$  atmosphere.

Fig. 5 illustrates the TEM image obtained from the sample which was subjected to 7-hour milling at 450 rpm milling rotation and then 2-hour annealing process under  $\text{NH}_3+\text{Ar}$  atmosphere at  $1300^\circ\text{C}$ . In TEM image in Figure 5.a, formation of bamboo-type BNNT was observed in the structure at the end of the annealing process. It is understood from the poor re-crystallisation of the nanotube structures that the milling process was not efficient. The diameter of this nanotube is approximately 100 nm. Figure 5.b illustrates another bamboo-type BNNT, and catalyst particle appears at the end part of the nanotube [12,13,14]. This nanotube formed in a very faulty manner. This situation indicates that the energy required to be acquired by the powder at 450 rpm did not reach to the sufficient level. This is because the core areas, which are necessary for the enlargement of the nanotubes, could not be exactly provided under milling conditions. Furthermore, TEM images are in accordance with XRD results. The number of nanotube product obtained is too low, the crystallinities of the tubes are not good and their diameters are large.



a)

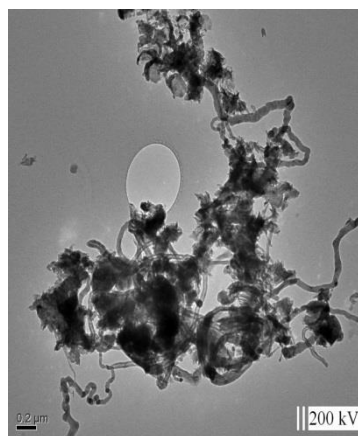


b)

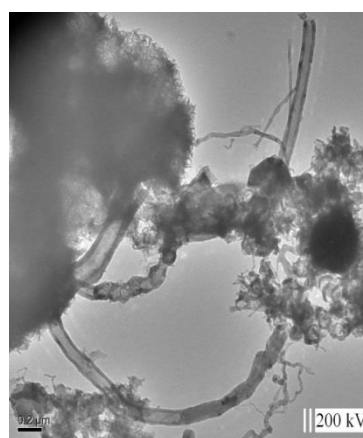
Fig. 5. a, b. TEM image of the sample with h-BN milled for 7 hours at 450 rpm under  $\text{N}_2$  atmosphere, and annealed for 2 hours at  $1300^\circ\text{C}$  under  $\text{NH}_3 + \text{Ar}$  atmosphere.

Fig. 6 illustrates the TEM image obtained from the sample subjected to milling process for 7 hours at 850 rpm of milling rotation and then annealing process for 2 hours at  $1300^\circ\text{C}$  under  $\text{NH}_3+\text{Ar}$  atmosphere. Fig.6.a shows presents BNNTs which exhibited a dense enlargement on the catalyst particles. These tubes were surrounded with non-transformed amorphous structures.

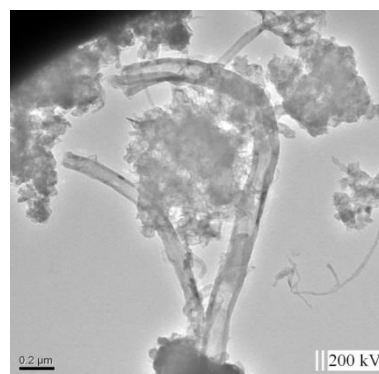
The diameters of the formed BNNTs are below 100 nm and their morphologies are parallel, multi-walled and cylindrical type [7,12]. Fig. 6.b presents BNNTs enlarging around an amorphous aggregate. The diameters of these nanotubes are below 50 nm and their lengths are at the level of a few microns. Their morphologies are parallel multi-walled cylindrical type and it was determined that their wall thicknesses are significantly higher than their internal gaps. This is a typical situation encountered in BNNTs. Due to their ionic bond structures; their inter-layer bonds are very strong. Very rarely, they are obtained in single walled form [6].



a)



b)



c)

Fig. 6. a,b,c. TEM image of sample with h-BN milled for 7 hours under  $\text{N}_2$  atmosphere at 850 rpm and annealed for 2 hours at  $1300^\circ\text{C}$  under  $\text{NH}_3 + \text{Ar}$  atmosphere.

Fig. 6c show present BNNTs which exhibited growth from nucleous area. The diameters of these nanotubes are about 100 nm. Their morphologies are parallel multi-walled cylindrical type. This BNNTs are proof effective milling.

Some researchers determined that as a result of milling, the presence of an amorphous structure (metastable) assists the tube for transformation [15].

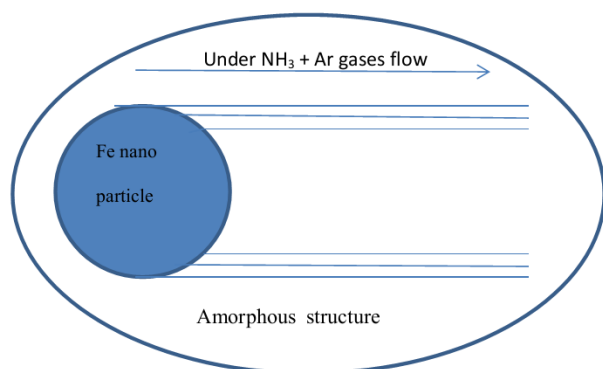
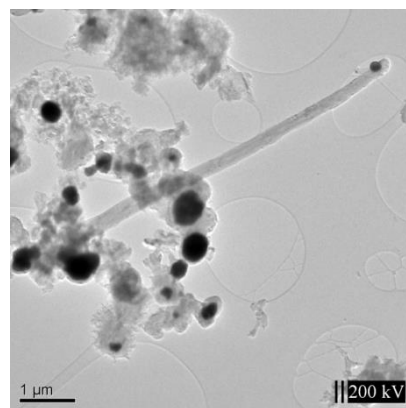
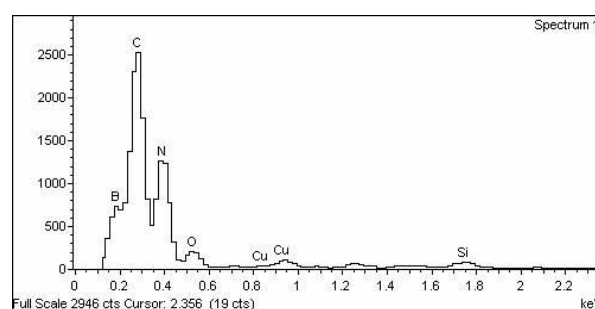


Fig. 7. Growth model of a boron nitride nanotubes [18].

Fig.7 illustrates amorphous BN, which degrades to nano size, needs to be in an aggregated form so to cover the surface of catalyst particle (Fe) in order to form Nanotube at the first stage of the reaction [16]. At this first stage, core areas constitute the suitable centres for structure formation. At high temperatures, atom mobility relatively increases and since the rate of fault in the structure is considerably high, the volume and surface activate the diffusion mechanism [17]. When the amorphous BN phases in the structure are heated, they act as free atom source and while the nano Fe particle diffuses inwards, the nitrogen atoms firstly separate from ammonia on the Fe surfaces and then diffuse into nano Fe particle. Nitrogen atoms move inside the walls of spherical particle and combine with boron atoms in the interfaces of amorphous structure. This consistent combination continues until boron ends in the solid particle [18,19]. Thus, BN shells form up around the catalyst particle, enlarge and thereby creating BNNTs. Under the scope of this process, BNNTs start to be formed throughout the interfaces of BN shells covering the catalyst particle by solid state diffusion. This enlargement mechanism is a result of solid state process [5,6,8,].



a)



b)

Fig. 8. a) TEM image of sample with h-BN milled for 7 hours under  $N_2$  atmosphere at 850 rpm, added with at.2 % catalyst and annealed for 2 hours at  $1300^\circ C$  under  $NH_3+Ar$  atmosphere b) EDS analysis taken from the Nanotube walls in the figure.

Fig.8.a illustrates a BNNT enlarging on the catalyst particle within the scope of above mentioned solid state process. One can see the catalyst Fe particles left in the structure since they could not provide proper conditions around the nanotube formed. The morphology of the nanotube is multi-walled parallel and cylindrical. According to result of the EDS taken over the walls of the nanotube in Figure.8.b, the dominant composition is B-N. Cu and C is due to the carbon coated Cu grid. Si and O are considered to pass from the study environment to the products during the experiments.

#### 4. Conclusion

h-BN starting material was grinded under different milling rotations and for different periods under  $N_2$  atmosphere and then annealed at  $1300^\circ C$  for 2 hours under  $NH_3+Ar$  atmosphere. BNNTs of different diameters and lengths were obtained in the products. Crystallinities, sizes and numbers of BNNTs formed varied based on the milling conditions. In milling process; when the milling rotation was selected as 850 rpm, BNNT production was ensured in desired efficiency. However, for 450 rpm, the desired number of BNNT product could not be obtained and it was concluded that in case this rotation is selected, longer milling periods needs to be reached.

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### References

- [1] S. Iijima, *Nature*, **354**, 56 (1991).
- [2] A. Rubio, J.L. Corkill, M.L. Cohen, *Phys. Rev.*, **B49**, 5081 (1994).
- [3] N.G. Chopra, R.J. Luyken, K. Cherrey V.H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, *Science*, **269**, 966 (1995).
- [4] Y. Chen, M. Conway, J.S. Williams, J. Zou, *J.Mater. Res.*, **17**(8), 1896 (2002).
- [5] Y. Chen, J. Fitz Gerald, J.S. Williams, S. Bulcock, *Chem. Phys. Lett.*, **299**, 260 (1999).
- [6] Y. Chen, J.S. Williams, *Synthesis Of Boron Nitrides Nano Tubes Using A Ball-Milling And Annealing Method*, *Nano Engineering and Structures Functional and Smart Materials*, p. 82, 2006
- [7] Y. Chen, C.P. Li, H. Chen, Y. Chen, *One imensional nanomaterials synthesised usinh high energy ball-milling and annealing process*, *Science and technology of advenced materials*, p. 839, 2006.
- [8] H. Zhang, Y. Chen, *Boron Nitride Nanotubes: Synthesis and Structure*, Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, Australia, 2000
- [9] C. Suryanarayana, *Progress İn Materials Science*, **46**, 1 (2001).
- [10] Y. Chen, T.C. Lewis, F. J. Gerald, J.S. Williams, *Applied Physics Letters*, **74**, 2960 (1999).
- [11] Y. Chen, F. Gerald, J.S. Williams, S. Bulcock, *Chemical Physics Letters*, **299**, 260 (1999).
- [12] J. Fengqiu, C. Chuanbao, X. Hong, Y. Ziguang, *Chinese J.Chem. Eng.*, **14**(3), 389 (2006).
- [13] J. Yu, C. Bill, P. Li, J. Zhou, Y. Chen, *J. Mater. Sci.*, **42**, 4025 (2007).
- [14] L.T. Chardderton, Y. Chen, *Phy. Let.A.*, **263**, 401 (1999).
- [15] Y. Chen, M. Conway, J.S. Williams, *Large-Quantity Production Of High-Yield Boron Nitride Nanotubes*, Department Of Electronic Materials Engineering, Research School Of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia, 2002.
- [16] L.T. Chadderton, Y. Chen, *Journal Of Crystal Growth*, **240**, 164 (2002).
- [17] R. M. German, *Sintering Theory And Practice*, Joyn Wiley & Sons. Inc., USA, 1996.
- [18] O.A. Louchev, T. Lauda, Y. Sato, H. Kenda, *Journal Of Chem.Phy.*, **118**, 7622 (2003).
- [19] T. Lauda, *Boron Nitride Nanotubes Grown Bynon-Ablative Laser Heating: Synthesis, Characterization,Growth Processes*, Phd, University Of Tsukuba, Japan, 2001.
- [20] Ö. Güler, E. Evin, *Optoelectron. Adv. Mater.-Rapid Comm.*, **6**(1-2), 183 (2012).

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