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Low temperature synthesis of nano-crystalline h-boron nitride from boric acid/ urea precursors

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Nano-crystalline hexagonal-boron nitride (h-BN) have promised a broad range of interesting applications due to its unique characteristics. In this work, nano-structured h-BN has synthesized by a low temperature-one step reaction of completely dissolved solution of commercial and low cost boric acid and urea fertilizer. Effect of different concentrations of urea, reaction atmosphere (air-N₂) and firing temperature (600, 800 °C) on the production of h-BN and type of yield were investigated. The formation of hexagonal boron nitride was proved from the binding energy for boron and nitrogen obtained from the X- ray photoelectron spectrum (XPS). The structural phase of the product was confirmed by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and differential thermal analysis (DTA). Transmission electron microscopy (HRTEM) has revealed the nano structure nature of the synthesized boron nitride. The results indicated that, nano-crystalline h-BN with a crystallite size of ≈ 4.5 nm has formed at low temperature of 800 °C. Moreover, a good thermal stability and oxidation resistance of h-BN can be synthesized with low cost and at low temperature in the nanoscale and has high potential to be used in advanced applications.

Key words : H-BN, XRD, XPS FT-IR, DSC, FESEM , HRTEM.

Introduction

Hexagonal boron nitride (h-BN) is considered as one of the most important unique ceramic materials that have brought a great concern due to its appealing characteristics. H-BN is III-V compound with a structure very similar to graphite and has been referred to as "white graphite". It is a layered structural material with a weak van de Waals interaction between the layers. Within each layer, its honeycomb structure is composed of alternating boron and nitrogen atoms instead of all carbon atoms, as in the graphene. H-BN is an electrical insulator with a direct band gap (5.97 eV). It possesses attractive high temperature properties such as, high melting point, high thermal conductivity, low thermal expansion coefficient, good thermal shock resistance, chemical inertness, excellent hardness and mechanical strength, corrosion and oxidation resistance, low density and microwave transparency [1-4].

After the discovery of the carbon nanotubes and their enormous application potentials beside the significant interest generated by nanostructured ceramic materials, Nano structured h- BN has received a great attention due to its attractive properties and its similarity in nanostructural form with the carbon nanotubes [5].

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Due to its unique and attractive combined properties, h-BN ceramics are of great interest for industrial applications as well as for materials science. These properties make it suitable for a huge variety of applications in the electronic industry, e.g. as substrate for semi-conductor parts, microwave transparent windows, for optical and magneto-optical recording media and for optical and disc memories. It has electrochemical applications including catalysts carries in fuel cells, electrodes in a molten salt fuel cell and structural materials for seals in batteries. It is used as lubricants (liquid and solid), fillers, moulds for hot pressing of ceramics, neutron absorbers and shields for nuclear reactors and components for high-temperature electric furnaces, coat in the iron and steel industry to enhance the corrosion resistance as well as to reduce the wear resistance on sliding parts like the crankshafts for compressors, break rings in continuous casting of steel, nonferrous industry (crucibles, tubes, plates), seal rings for gas sensors, insulators and source holders for ion implantation systems, furnace vents, stacks and fixtures, welding tips for plasma arcs, sintering aid and refractory ceramics. Its composites with nitride is used to dope silicon wafers, for heat exchangers, nozzles in continuous steel casting, for integrated package materials in the electronic/electrical industry. Its composites with boride and carbide are used as evaporator crucibles and boats for vacuum metallization of plastics, paper textiles and glass [6-8]. Moreover, h-BN reduce the thermal expansion and friction coefficients, increases

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thermal conductivity, improve thermal shock resistance and machinability and use temperatures of polymer matrix composites [9]. Because of the great importance and the increasing consumption of h-BN, searching for cost effective and low temperature production methods becomes a necessary and a challenge.

Various methods have been developed for the synthesis of h-BN. Traditionally, h-BN is prepared by high temperature synthesis methods, including the reaction of boron containing compounds (boric acid, boric oxide, borates of alkaline earth metal) with nitrogen containing compounds (amides, cyanides, cyanimides, urea and thiocyanates) at a temperature of 1600 °C or higher [10-15]. However, due to the low melting point of boron compounds and the excessive oxygen, inert fillers such as tri-calcium phosphate (Ca₃(PO₄)₂) and carbon additions were used [16].

In addition, several other methods have been proposed for the preparation of h-BN; direct nitridation of the pure boron element at high temperatures, the vapor phase reaction between boric oxide and ammonia at 800 °C-2400 °C, and the reaction of alkali metal borides or alkaline earth metal borides with silicon and/ or aluminum or their alloys at a temperature between 200 - 1200 °C in nitrogen atmosphere.

Moreover, carbothermal reactions were successfully used for synthesis of h-BN. In this technique, boric acid or borates is reduced by carbon then heat treated in a nitrogen atmosphere at 1200-1500 °C in the presence of calcium carbonate and manganese catalysts to enhance the yield [17].

Carbothermic decomposition of polymeric precursors containing B-N boranes such as (amino and amine) and borazines are considered a potential candidate for producing high purity BN powder. On the other word, for special synthesis of nanostructured h-BN, laser ablation, arc discharge, chemical blowing, chemical vapor deposition, carbothermal reduction of B_2O_3 and B_4C , microwave assisted solid state synthesis, arc melting and other novel methods have been developed. However, from a commercial and complexity points of view, these above mentioned methods have certain limitations to produce h- BN in an economical way [18].

Additionally, most techniques used to produce the nanostructured h-BN are conducted at high temperature (>1000 °C), complicated and expensive. Therefore, low temperature synthesis of nanocrystalline h-BN powders should be investigated.

In this paper, a low cost synthesis of nanocrystalline hexagonal boron nitride was investigated for the first time by the single step reaction of commercial boric acid and urea fertilizer at low temperature (600 & 800 °C). Effect of different concentrations of urea, reaction atmosphere (air- N_2) and firing temperature on the production of h-BN and type of yield were studied. The phase composition, thermal analysis, and microstructure of these compositions were detected

using X-ray diffraction (XRD), X- ray photoelectron spectrum (XPS), differential thermal analysis (DTA), infrared spectrum (IR), scanning electron microscope (FESEM) as well as transmission electron microscope (TEM).

Materials and Experimental Procedures

Materials and processing

Commercial boric acid (H_3BO_3) and urea fertilizers (CO $(NH_2)_2$) were used as starting raw materials. Chemical analysis of urea by Inductive coupled plasma (ICP-OES, OPTIMA 2000 DV Perkin Elmer, USA) indicated its containment of about 0.13 wt% magnesium.

Mixtures of boric acid and different concentrations of urea with a mole ratio of 1:2, 1:4 and 1:6 were completely dissolved in deionized water to give solution with high homogeneity. The different mixed solutions were dehydrated and powdered at 80 °C in an oven drier. In order to obtain nanocrystalline h-BN ceramics, different controlling parameters have been studied as different reaction atmospheres (air-N₂) and temperatures (600, 800 °C). So that, the dried white precursors of the three mixtures are placed in alumina crucibles separately and heat treated at different temperatures under nitrogen and air atmospheres in a muffle furnace. Three different firing schedules or regimes were applied. The mixtures were heated up to 600 °C with a dwell time of 2hrs and heating rate of 10 °C/min under nitrogen atmosphere with a flow rate of 1.5 L/min (first regime). In the second heating program, the mixtures were heated up to 600 °C for 2hrs with heating rate of 10 °C/min in air without N₂ flow, then followed by nitrogen gas flow (1.5 L/min) and heating up to 800 °C(10 °C/min) for 3h (last regime). Last program is similar to the first one; however the mixtures were heated up to 800 °C for 3hrs.

The obtained products of each mixture at each firing program were collected and washed with hot deionized water followed by dilute nitric acid for several times in order to remove the impurities. Finally the mixtures were washed three times with absolute ethanol to remove water. The final product was dried at 60 °C for 12 hrs and collected to be characterized by various techniques.

Characterization

XRD patterns of the resulting products were characterized by a Brucker D8-advance X-ray powder diffractometer with Cu Ka radiation (k = 1.5406 Å). The crystallite sizes of the produced boron nitride were calculated from the X-ray diffraction data using the Debye-Scherrer formula:

$$d_{RX} = K\lambda/\beta \cos\theta \tag{1}$$

Where d_{RX} is the crystallite size, k = 0.9 is a correction

factor to account for particle shapes, β is the full width at half maximum (FWHM) of the most intense diffraction peak plane of h-BN phases, λ is the wavelength of Cu target = 1.5406 Å, and θ is the Bragg angle.

X-ray photoelectron spectra (XPS) was recorded on a K- α instrument (Thermo Scientific, England) using monochromated, micro-focused Al Ka radiation as the excitation source.

Fourier transform infrared spectra (FTIR) spectroscopy (Model, Jasco-6300 type A, Japan spectrometer) was used at room temperature in the range of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹. It has been used to confirm the formation of the produced compounds.

Differential thermal analysis/thermogravimetric analysis (DTA-TG) of the ultimate product was performed using a DTA-TG analyzer (Model, NETZSCH STA 409 C/CD, Germany) in flowing air (50 ml/min) up to 1000 °C at a heating rate of 10 K/min.

Powder morphology and microstructure of the obtained products were examined by using backscattered electron (BSE) in the field emission scanning electron microscopy (FESEM; QUANTA FEG 250, Holland) and high resolution transmission electron microscope (HR-TEM). TEM samples were prepared by dispersing the powders in acetone. Ultrasonic oscillation for 1 h was introduced to decrease the aggregation followed by placing a drop of the suspension on holey carbon film supported on copper grids. For TEM and SAED analysis, we used (HR-TEM; JEM- 2100, Japan).

Results and Discussion

XRD patterns of different mixtures (1:2, 1:4 and 1:6) of boric acid and urea fired at 600 °C/2hr in N₂ atmosphere are shown in Fig. 1. It was found that an amorphous phase structure was formed for all mixtures. However, the convex hump centered at twotheta positions of (25° to 27°) may refer to (002), the most known and intense plane of h-BN [19]. In order to confirm the formation of amorphous BN, XPS analysis was carried out on 1:2 mixture of boric acid and urea to identify its chemical composition Fig. 2. The survey scan contains peaks from boron, nitrogen and adventitious carbon as well as oxygen. The C 1s spectrum is located at 285.01 eV which indicates the presence of C impurity. This may be attributed to the adsorption of CO_2 on the surface of the sample. The high resolution spectra for B 1s and N 1s regions are shown in Fig. 2(a) and 2(b) respectively. It was concluded that, the peaks located at ≈192 eV and ≈398 eV and ascribed to B 1s and N 1s respectively, correspond to the binding energies responsible for B-N bond formation [20]. Thus, it was confirmed that the amorphous phase formed by firing different boric acid and urea mixtures at 600 °C/2hr in the N2 is amorphous boron nitride (a-BN) and further temperature increase



Fig. 1. XRD patterns of different boric acid and urea mixtures fired at 600 $^{\circ}$ C/2 hr in N₂.



Fig. 2. XPS survey spectrum of 1:2 mixtures fired at 600 $^{\circ}$ C/2 hr in N₂.

may lead to the formation of h-BN.

According to previous works [21], the a-BN is formed as a result of firing a mixture of boric acid and urea in the temperature range 500-600 °C. When the mixture heated in the temperature range 250-300 °C, ammonium polyborates $(NH_4)_2B_4O_7$ is formed. Additionally, part of urea in the reaction reacts with the water produced to form ammonia. Finally, by heating upon 500-600 °C, the ammonium polyborates reacts with ammonia forming the a-BN according to the following equations:

$$4 \cdot H_3 BO_3 + CO \cdot (NH_2)_2$$

$$\rightarrow (NH_4)_2 B_4 O_7 + CO_2 + 4H_2 O$$
(2)

$$CO \cdot (NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$
(3)

$$(NH_4)_2B_4O_7 + NH_3 \rightarrow 4 \text{ a-BN} + 7 \text{ H}_2O$$

$$\tag{4}$$

XRD patterns of different boric acid and urea mixtures fired at 600 °C/2hr in the air are illustrated in Fig. 3. As



Fig. 3. XRD patterns of different boric acid and urea mixtures fired at 600 $^{\circ}$ C/2 hr in air.



Fig. 4. XRD patterns of different boric acid and urea mixtures after increasing temperature form 600 $^{\circ}$ C/2 hr in air to 800 $^{\circ}$ C/3/hr in N₂.

shown, the three different mixtures of boric acid and urea have followed the same behavior and gave the same XRD phases' pattern. Different fired mixtures gave ammonium pentaborate tetrahydrate (ABH) when fired at air. However, by a further increase of the firing temperature to 800 °C /3hr with nitrogen gas flowing, the ammonium borate hydrate phase that formed in all three mixtures fired in the air has completely transformed into hexagonal boron nitride as indicated in Fig. 4. By using the Debye-Scherrer formula, it was found that the produced boron nitride (BN; JCPDS card no 73-2095) has nanocrystalline nature with very fine crystallize size of 4.5-5 nm. The three identified peaks of the produced powders appeared at 2θ values of 26.74°, 41.61° and 55.10°. These peaks correspond to [002], [100] and [004] diffraction planes of the BN phase, which described based on the patterns as a hexagonal phase with space group: P63/mmc. The refinement gives the cell constants (a = 2.504 Å, c = 6.661 Å) which is consistent with the value reported in literature (a = 2.504 Å, c = 6.656 Å). Moreover, the peaks broadening of the h-BN were occurred due to the small grain size of the formed powders and confirm that the grain size of the samples is on the nanometer scale.

On the other hand, the conversion of ABH to h-BN upon increasing temperature to 800 °C and nitrogen gas



Fig. 5. XRD patterns of different boric acid and urea mixtures fired at 800 $^{\circ}$ C/2 hr in N₂ without presence of any other impurities.

flowing can be attributed to the decomposition of ABH into NH₃, H₂O gases and B₂O₃. At the heating temperature 800 °C, B₂O₃, NH₃ and Mg (present in urea) can be reacted with each other to form BN. The N₂ gas flowing could be helpful for enhancing the reaction rate and reducing the reaction temperature. The presence of magnesium could be helpful for the reduction of boron oxide to boron metal which in turn reacted with nitrogen to form BN according to the following equations:

$$2NH_4.B_5O_8 \cdot 4H_2O \to 5B_2O_3 + 2NH_3 + 9H_2O$$
 (5)

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO \tag{6}$$

$$2H_2O + Mg \rightarrow Mg (OH)_2 + H_2$$
(7)

$$Mg (OH)_2 \rightarrow MgO + H_2O$$
(8)

$$2B + NH_3 \rightarrow 2BN + 3H_2 \tag{9}$$

Finally, The XRD patterns of the different boric acid and urea mixtures fired at 800 °C/3hr in N₂ atmosphere are given in Fig. 5. It can be inferred that, firing the different mixtures of starting materials at such conditions gave directly the hexagonal BN ceramics with a nanocrystallite size of 4.5 nm in one single step reaction. The XRD patterns of these samples gave the same interplanar d-spacing values and XRD diffraction planes ([002], [100] and [004]) of samples fired from 600-800 °C in N₂, Fig. 4. There are no impurity peaks such as B, B₂O₃ were detected in the XRD patterns. This indicates the complete conversion of the starting boric acid and urea in into the h-BN ceramics.

From these results, it can be concluded that, direct firing of boric acid and urea mixtures at 800 °C/3 hr in N_2 atmosphere is sufficient for obtaining fully crystallized nano h-BN with the most intense and known peak [002] with low cost method, low temperature and without using any catalysts.

In an investigation of the influence of urea different concentrations on the weight loss and the yield

 Table 1. Weight loss % of boric acid and urea with different mole rations.

Mole rations	Wt loss %
1:2	80.6
1:4	88.34
1:6	91.2

Table 2. Yield % of h-BN after washing with hot water and HNO_3 .

Mole rations	Yield %
1:2	25
1:4	14.6
1:6	6.5



Fig. 6. XPS survey spectrum of 1 : 2 mixture fired at 800 °C/3 hr in N_2 .

percentage of the produced h-BN, it was found that urea concentration has a major role in the weight loss and yield of the final product. Increasing urea concentrations have led to increasing the weight loss and decreasing the yield percentage of the produced h-BN as illustrated in Table 1 & 2. The boric acid and urea mixture of 1:2 mole ratio gave the highest yield and lowest weight loss and is chosen as the optimum one for the further characterization.

In order to investigate and confirm the elemental compositions, chemical bonding states and impurities of the produced h-BN, XPS analysis of 1:2 mixture of boric acid and urea fired at 800 °C/3 h in N₂ is given in Fig. 6. The survey spectrum of the sample inferred the presence of boron, nitrogen, oxygen and a small amount of carbon with binding energies of N 1s, B 1s, C 1s and O 1s at 398.85, 191.12, 285.19 and 532.97 eV, respectively. The quantitative analysis of the C and O peaks indicates that the ratio of C/O is approximately 1:2. The two peaks can be attributed to the adsorbed carbon dioxide on the surface. The B 1s peak located at 191.12 eV and the N 1s peak formed at 398.85 eV indicates the formation and existence of a B-N bond, which in good agreement with those in the literature [22, 20]. The quantification of B 1s and N 1s



Fig. 7. FT-IR spectrum of 1:2 mixture fired at 800 °C/3hr in N₂.



Fig. 8. DSC and TG of synthesized nanocrystalline h-BN.

peaks confirmed that the atomic ratio of B: N was 1:1.03, which closely agrees with the stoichiometric composition of h-BN. Hence, it was confirmed that the phase formed by single step firing of 1:2 boric acid and urea mixture at 800 °C/3 h in N_2 is hexagonal boron nitride (h-BN) without the presence of any other impurities.

The FT-IR spectrum at 400-4000 cm⁻¹ for the nanocrystalline h-BN produced from firing 1:2 boric acid and urea mixture at 800 °C/3h in N2 is demonstrated in Fig. 7. Two strong characteristic peaks located at 1389 and 774 cm⁻¹ could be observed clearly. The peak formed at 1389 cm⁻¹ has been assigned to the in-plane B-N stretching vibrations of the sp²-bonded h-BN that is completely differ from vibrations of sp³ of cubic phase c-BN which confirms the formation of h-BN [23]. On the other hand, the other peak located at 774 cm⁻¹ is due to the B-N-B bending vibrations. Peak formed at around 3375 cm⁻¹ is due to the -OH vibration arises from the H₂O released from the h-BN crystallite formation. The broad absorption peak at 3158 cm⁻¹ is an overlap of N-H stretching vibrations and O-H vibrations due to the moisture absorbed on the surface of the sample. The small peak observed at 1106 cm⁻¹ is probably due to the presence of some surface bonds containing boron and/or nitrogen or could be due to a C-B bond [24].

In order to investigate the thermal stability and the oxidation resistance of the obtained nanocrystalline h-BN, the nanocrystalline h-BN powders synthesized by



Fig. 9. FE-SEM of synthesized nanocrystalline h-BN.

the single step reaction of completely dissolved solution of boric acid and urea at 800°C /3hr in N2 are subjected to thermogravimetric (TG) and differential thermal analysis (DTA) (Fig. 8) up to temperature of 1050 °C in air with heating rate 10 K/min. It can be observed that in the range of RT-300 °C, two endothermic peaks located at ~60 and 180 °C in DSC curve with a mass loss of about ~11% appear which can be attributed to the evaporation of physisorbed moisture on the surface of the sample. There was no massive change in the weight of the produced h-BN with increasing temperature to 900 °C. However, by increasing temperature above 950 °C, an obvious weight gain was observed of about ~11.75%. This can be corresponded to the extensive oxidation of h-BN into B₂O₃ and nitrogen oxide [25]. Moreover, this oxidation can be confirmed by the outstanding and sharp exothermic peak formed between 950 and



Fig. 10. TEM of synthesized nanocrystalline h-BN, (a) TEM images, (b) HR-TEM of lattice plane, (c) SAED patterns.

1000 °C and centered at about at the ~ 994 °C in the DSC curve. Finally, at a temperature of 1000 °C, the weight gain due to the h-BN oxidation starts to decrease due to the extensive evaporation of the B_2O_3 at this temperature as observed in Fig. 8 [26]. This indicates that, the synthesized nanocrystalline h-BN possess a very good thermal stability and oxidation resistance at high temperature (up to 900 °C).

Microstructure investigation of the produced nanocrystalline h-BN fired at 800 °C/3hr in N2 atmosphere is obviously revealed by FE-SEM, Fig. 9. Generally, a large number of nano h-BN aggregates can be observed, Fig. 9(a). This degree of stacking and agglomeration is owing to the high crystallinity nature and the ultra-fine size of the obtained h-BN despite of its processing without using any catalyst. It was observed that the formed h-BN was homogeneously distributed reflecting the homogeneous mixing of the starting materials. In addition, the produced BN powder possessed angular grain structure with has a flake like form and hexagonal shape, Fig. 9(b) which is due to the intrinsic crystal structure of the h-BN. Moreover, it is also possible to observe and notice the layered sheet structure of the produced BN which indicates the full crystallization and confirms formation of the nanocrystalline h-BN, Fig. 9(c).

The TEM images, HR-TEM of lattice planes and

SAED of self-agglomerated h-BN fired at 800 °C for 3hrs in N_2 are shown in Fig. 10. The morphology shows a bunch of very fine nanocrystals self-organized to form a bigger cluster. Images confirm nanoscale of the synthesized boron nitride samples and formation of hexagonal fine grains structure, Fig. 10(a). In addition, the visibility of the clear and parallel lattice fringes observed by using HR-TEM indicates the high crystalline nature of the sample. Due to the stacking and agglomeration of crystal lattices, plane image of the samples gave images similar to the fingerprint pattern as observed in Fig. 10(b). The spacings of 2D lattice fringe (3.33 and 1.6 Å) of the obtained nano-BN powder corresponds to the indices of the hexagonal BN planes [(002) and (004)] with P63/mmc symmetry. These results are totally agreeing with the XRD patterns of the h-BN. Moreover, the selected area diffraction (SEAD) pattern of the synthesized boron nitride powders gave a single hexagonal crystal pattern, Fig. 10(c). It also confirms the crystallinity of BN, in which the diffraction ring diameters (002) and (004) are corresponding to the hexagonal BN structure.

Conclusions

Single nanocrystalline h-BN powders were successfully synthesized by a cheap, simple and low temperature-one step reaction method of completely dissolved solution of commercial and boric acid and urea fertilizer. Different parameters affecting on the production of h-BN has been investigated, such as the effect of different concentrations of urea (1:2, 1:4 and 1:6), reaction atmosphere (air- N_2) and firing temperature (600, 800 °C). It was found that, increasing urea concentrations have led to increasing the weight loss and decreasing the yield percentage of the produced h-BN. The boric acid and urea mixture of 1:2 mole ration gave the highest yield and lowest weight loss has chosen as the one. Furthermore, firing temperature and nitrogen gas flowing have played a key role in producing h-BN ceramics. Ultrafine hexagonal BN powders (≈4.5 nm) were produced by firing 1:2 boric acid and urea mixture at 800 °C for 3hrs in N₂ without using any catalysts or additives. The results suggest that, h-BN with very good thermal stability and oxidation resistance can be synthesized with low cost and at low temperature in the nanoscale and has high potential to be used in advanced applications.

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