Lowering Synthesis Temperature of hBN by Improvement of Precursor

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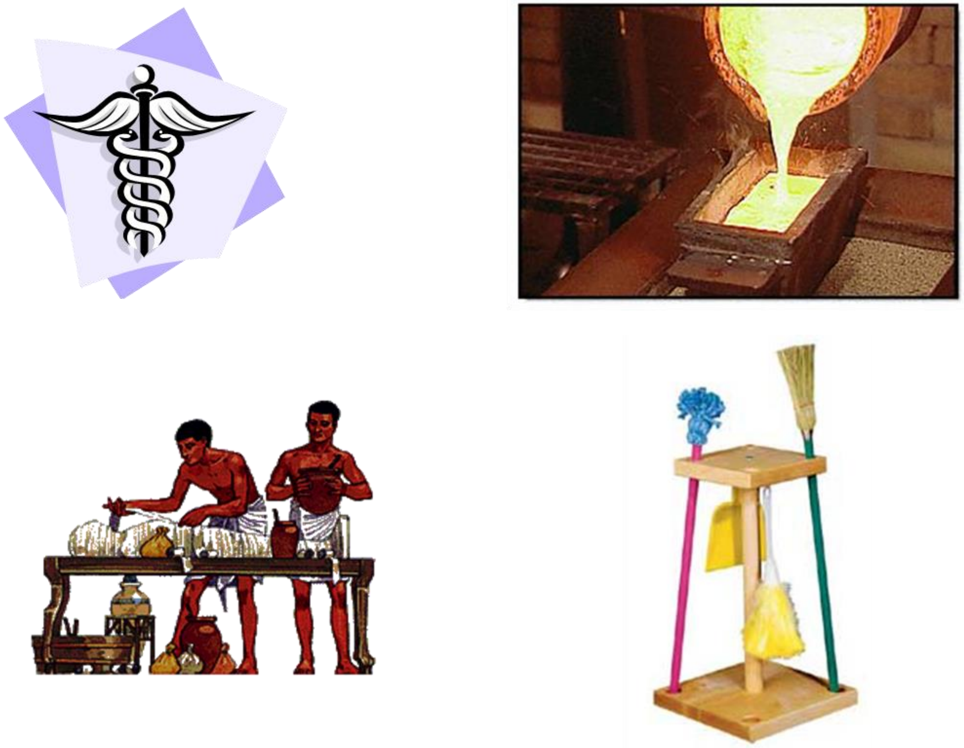
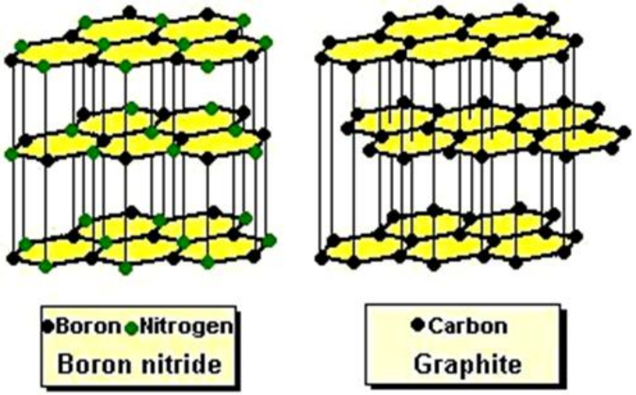
INTRODUCTION

Boron compounds, especially borax, have been used for more than thousand years by Babylon, ancient Egypt, and ancient Greek for cleaning, melting valuable jewels, mummifying, and curing illness.



INTRODUCTION

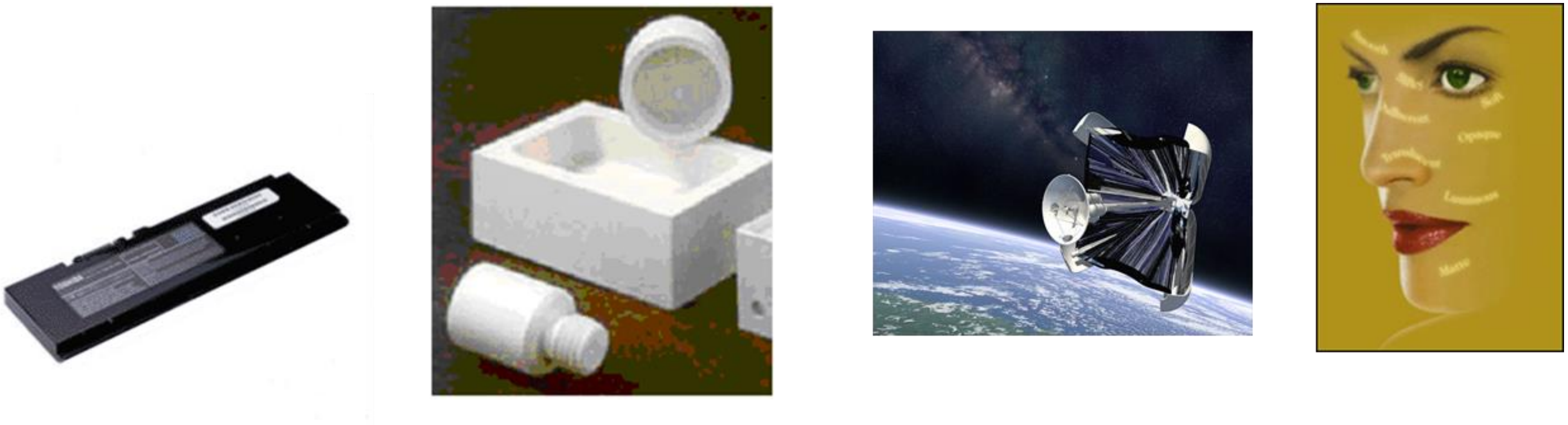
Boron nitride is one of the oldest known boron-nitrogen compounds, reported in 1842. Hexagonal boron nitride (hBN) is a typical layered substance, as planar hexagonal networks are stacked with van der Waals force to form a three-dimensional, graphite-like structure.



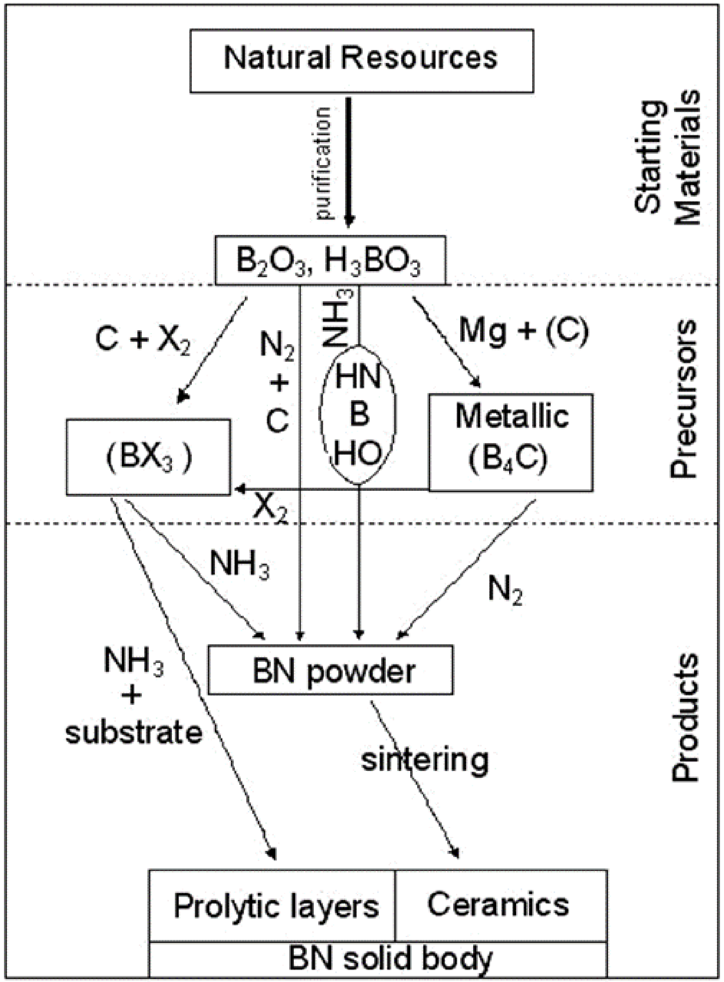
INTRODUCTION

Boron nitride is an extraordinary structure in the area of materials science. Due to the special bonding behaviors of boron and nitrogen, BN exists in many different phases.

hBN, is a non-oxide advanced ceramic material and it has excellent physical and chemical properties as low density, high thermal stability and conductivity, high melting point, low dielectric constant, chemical stability, machinability and neutron capturing. These characteristics are the reason why BN is valuable in many applications, especially in the area of technical ceramics.



INTRODUCTION



The routes of synthesis of BN.

Although there are a lot of methods to produce hBN, principally two reactions are used on the industrial scale:

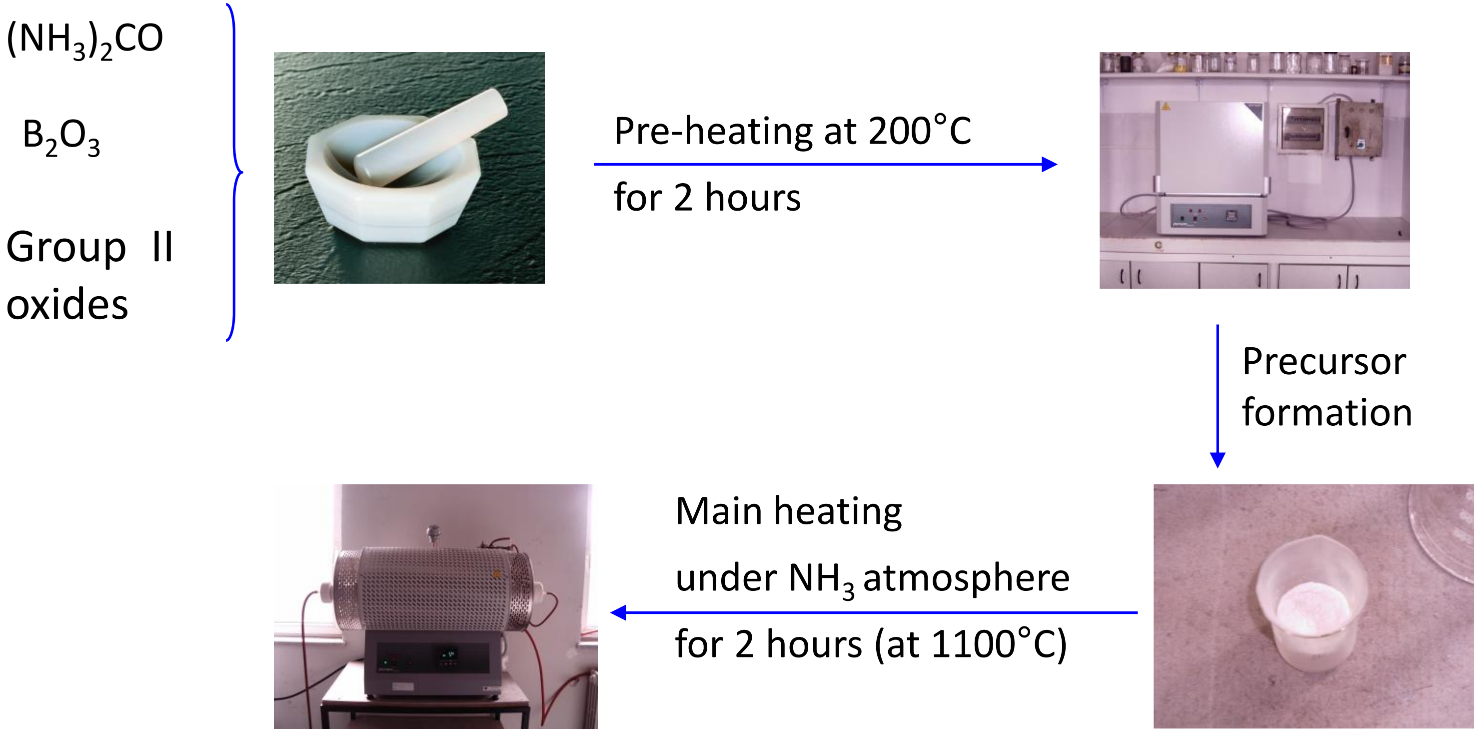
1- The reaction of boric acid and ammonia in the presence of carrier substances ($Ca_3(PO_4)_2$, CaO, etc.) at 1500°C and above and

2- Heating of boric acid and nitrogen containing organic compounds such as melamine, urea, and dicyanamide etc., up to 2100°C under nitrogen atmosphere.

Both methods are classical high temperature solid state synthesis and high temperature is necessary for the inorganic solids because of their low diffusion coefficient.

EXPERIMENTAL

The modified O’Connor method was used for hBN synthesis.



$(NH_3)_2CO$

B_2O_3

Group II oxides

Pre-heating at 200°C

for 2 hours

Precursor formation

Main heating

under NH_3 atmosphere

for 2 hours (at 1100°C)

The product was boiled in 10% HCl solution, leached in ethanol and dried in an oven at 100°C.

RESULT AND DISCUSSION

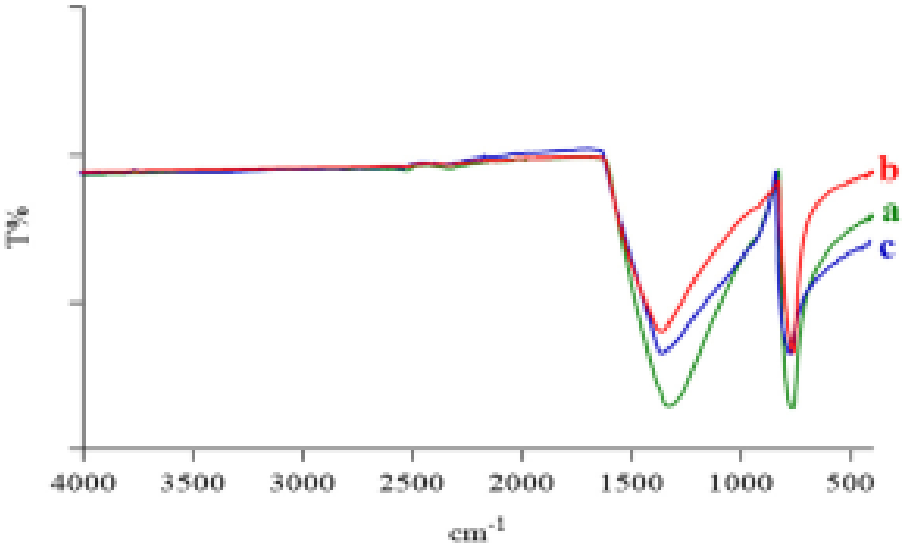
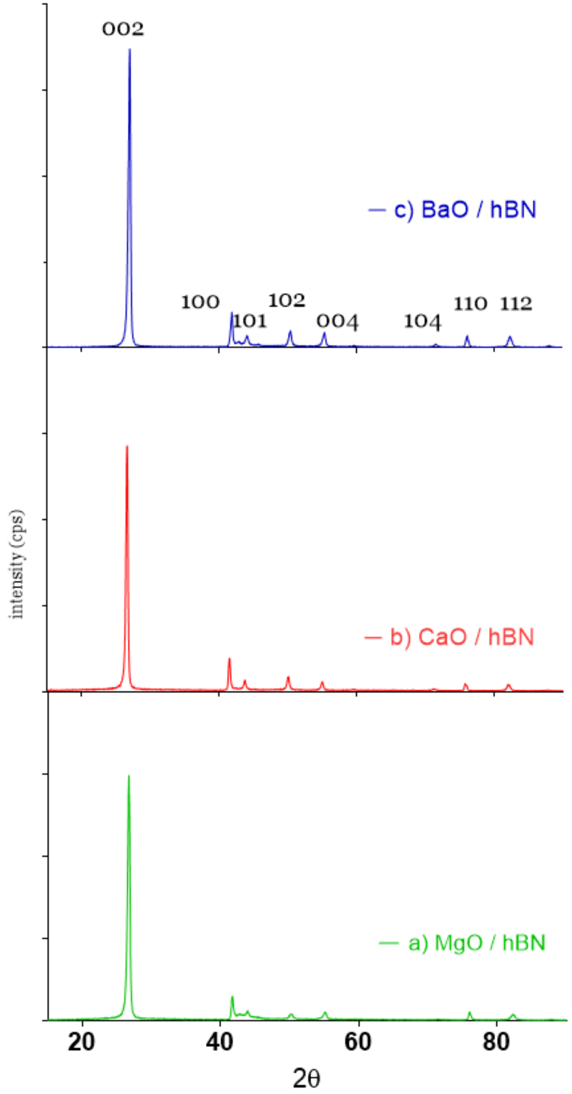


Figure 1 indicated that two strong characteristic peaks were labeled as BN in-plane and out-of-plane vibrations at ~1340 and ~761 cm^{-1}, respectively.

RESULT AND DISCUSSION



Crystal structure of the hBN samples were examined by XRD and the results were matched with ICDD card no: 34-421. No different phase which could be originated from Group II oxides and boron oxide were found. In diffractograms (Figure 2), all peaks ((002), (100), (101), (102), (004), (103), (104), (110), (112), and (006)) were labeled as hBN.

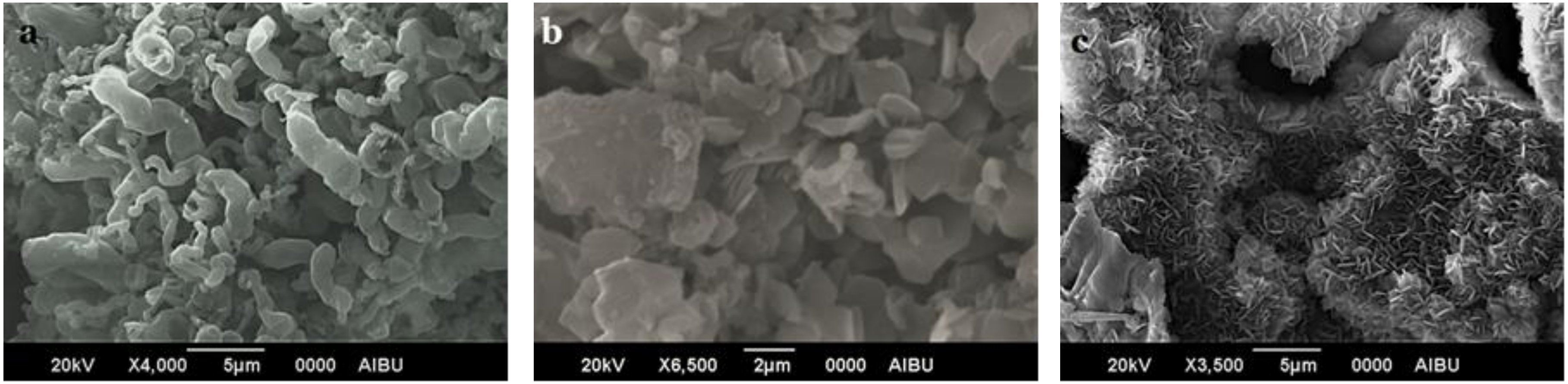
RESULT AND DISCUSSION

Table 1. Calculated lattice parameters, grain size, and graphitization index of hBN samples.

Metal Oxides	Lattice Parameter (in Å)		Grain Size (in nm)	Graphitization Index*
BaO	a_o	2.506	24	2.44
	c_o	6.700		
	d	3.350		
CaO	a_o	2.496	22	2.74
	c_o	6.602		
	d	3.301		
MgO	a_o	2.502	21	3.45
	c_o	6.664		
	d	3.332		

*The term "graphitization index" (G.I.) was used for estimating the degree of crystallization of the hBN.

RESULT AND DISCUSSION



SEM images of hBN samples at 1100 °C. a) MgO / hBN, b) CaO/ hBN, c) BaO/ hBN.

SEM images indicated that samples conglomerated and plate like crystals. The morphology difference of hBN may possibly be originated by different metal usage.

RESULT AND DISCUSSION

The use of both ammonia and metals lowered the formation temperature of hBN; metals act as catalysts and ammonia acts as a nitriding agent. Furthermore, the usage of metal salts grows boron oxide surface so that the full reaction of boron oxide and ammonia is possible. According to these statements and results of the previously presented FTIR and XRD analyses, Group II oxides play role as a catalyst, lowering the formation temperature of hBN and increasing crystallinity. Usage of BaO provided better result among the other oxides. It may be caused by low melting point and bigger atomic radius.

CONCLUSION

In summary, nano-sized hBN powders were synthesized at 1100 °C. In the industrial scale, hBN is produced above 1500°C, so that the synthesis temperature used in our study can be accepted comparatively low temperature. Group II oxides lowered the synthesis temperature of hBN by increasing the boron oxide and ammonia interaction. Also, metal oxides affected the morphology of hBN and G.I.

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