THINK INDIA JOURNAL
ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Routes of Synthesis of Binary Covalent Carbides: A Review

Nupur Prasad[1*]
[1]Lovely Professional University, Phagwara, Punjab, 144411, India.
*Email id: nupur.20362@lpu.co.in, Contact no: 7888996323

Abstract
SiC and B_4C are the only carbides, that show complete covalent character. These compounds exhibit several useful properties that can be employed in laboratories and industries. They have exceptional mechanical properties, show inertness towards environment, and have semiconducting behaviour, to name a few. Hence, efforts have been made to synthesise these compounds. Several routes of synthesise have been employed for this purpose. Further, work can be done in this direction to improve the processes and applicability of these materials.

1. Introduction:

Materials' synthesis is one of the most important aspects of chemistry. A chemist's key job is to synthesise materials of desired properties. This opens a huge up a door to learn and earn. Here, the routes of synthesis of truly covalent binary carbides is reviewed. Boron carbide and silicon carbides are the only true covalent carbides that exists in nature. Properties e.g. strong covalent bonds between atoms of these molecules, electronegativity, atomic radii, chemical inertness and extreme hardness make them useful for several applications [1-3]. Applications of materials depend upon the properties of materials which justifies the synthesis of that material. Hence, it is appropriate to discuss the properties and applications of any material before discussing the routes of synthesis of that material. This provides a logic why scientists are working to produce a material. Keeping this logic into mind it was believed that a short discussion on the properties and applications of SiC and B_4C is appropriate and are presented in sections 1.1 and 1.2.

1.1 Properties and applications of SiC:

SiC exists in different layered forms known as prototypes which forms amorphous, polycrystalline, and monocrystalline solids. The extraordinary mechanical properties e.g. stiffness, strength and toughness of SiC is attributed to its strong covalent bonds and very short bond length. Its chemical and thermal inertness makes it useful for several applications where high temperatures are required [4-5]. SiC nanomaterials are used to prepare mechanically strong composites [6-7]. Bulk SiC showed different electrical and optical properties than nanosized SiC [8-11]. Similarly, thermal conductivity of nanowires is significantly less than bulk SiC. It also shows effects like graphitization and ohmic heating [12-16]. Ultrahydrophobic or superhydrophobic surfaces form contact angles more than 150° are highly hydrophobic and the contact angles of a water droplet exceeds 150° which is known as 'Lotus effect' [17]. 1D SiC show excellent hydrophobicity. Several groups of scientists worked on wettability of SiC [18-20].

SiC is used for the fabrication of composites that can be used in extreme conditions e.g. very high temperatures [3-6]. Composites of SiC and titanium alloys as well as composites of SiC with aluminium alloys were prepared. Both these composites demonstrated much better mechanical and thermal properties than the original materials. These composites can be used in aerospace applications [21]. Although, this material shows very good mechanical strength, but cracks propagate in SiC nanowires [22]. Several other composites e.g. with poly(triazole-

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

imide) and copper powder of better tensile strength and thermal properties were synthesised [23-24]. Tyranno-fibres [25] of better quality were fabricated when it was reinforced with SiC nanowire [26]. Similarly, carbon/carbon composites were toughened by the introduction of SiC [27].

SiC fibres and SiC/SiC ceramic matrix composites (CMCs) was developed by NASA's Glenn Research Center [28]. In field emission electrons get ejected from its surface when exposed to strong electric fields. In the absence of electric field, this is a very difficult process as it requires lot of energy to eject electrons from a material [29]. Power electronics sector has huge demand of SiC [30-35]. It has several other applications e.g. in the fabrication of sensors [36], as catalyst [37-40], as microwave absorber [41], in bioimaging [42-44] and as biomaterials [45].

1.2 Properties and applications of boron carbide

Boron and carbon react to form a range of carbides from B_4C to $B_{10}C$. Although, electron precise (electron-precise compounds have the required number of electrons to write their 'Lewis electron dot structure') species $B_{12}C_3$ has never been isolated experimentally. Electron deficient $B_{13}C_2$ is reported to melt congruently at 2450 °C and 2480 °C, while the most electron-rich composition ($B_{12}C_3$) melts incongruently at 2350 °C and 2360 °C, indicating its comparative instability [46].

Covalent boron carbide (B_4C) grabs third position in nature as far as hardness of materials are concerned. Diamond holds first position and cubic boron nitride holds second position in this regard. The strong covalent bond makes it extremely hard as it has low density as well. Hence, can be used in unique applications where strength as well as hardness is required [47]. It is a very good electrical conductor as well although its low toughness, strength and poor damage tolerance limits its use. Efforts have been made to improve these properties for example by coating the pressed piece of B_4C was coated with BN [48]. Like SiC, B_4C is also used to prepare several composites e.g. aluminium metal was reinforced with B_4C [49]. Composite of B_4C with silicon were also prepared to improve its properties [50]. A range of composites were synthesised [51-53] e.g. hardness of aluminium-1100 matrix was increased by eleven folds when reinforced by 25% of B4C [51]. Range of composites were synthesised using this material [54-57] for example researchers working on Tribology [54] used composites of boron carbide with magnesium [55]. Few other applications of this material are in nuclear reactor [58-60], in the fabrication of Boral [61], as semiconductor [62-76].

The range of properties and applications of binary covalent carbides viz. SiC and B_4C shows clearly the need of their synthesis. Hence, several methods of synthesis have been developed. A review of routes of synthesis of binary covalent carbide is presented in the following paragraphs.

2.1 Synthesis of SiC:

The above discussed applications of SiC and B_4C showed that there is an utmost need of synthesis of these binary covalent carbides. Efforts have been made to synthesise these materials. In this section few methods of synthesis of SiC are discussed.

Synthesis of SiC using sol-gel route: Use of sol-gel synthetic route has several advantages. For example, it does not require highly sophisticated laboratory arrangement, it can be carried out at room temperatures or relatively lower temperatures than solid state synthesis, high-purity, good chemical homogeneity (to atomic scale) can be achieved and cost-effectiveness.

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

It also offers possibility forming films or fibers from gels which are of technological significance. Ehsani *et al.* used sol-gel route for the synthesis of β-SiC. β-SiC is a polytype of SiC. Tetra- ethoxysilane (TEOS), ethanol and water were mixed to form a sol. Phenolic resin was added to this sol. Ammonium polycarboxylate was used as dispersant. It was then dried to from a powder which was then pyrolyzed at higher temperatures to form the desired product.

Silicon carbide nanopowders and nanowhiskers were synthesised using organic substances e.g. phenolic resin as one of the starting materials. Silicon alkoxide was also used as one of the reactants. Laser particle size analysis showed narrow size distribution of particles [77].

In another attempt, silicon carbide was synthesized using Stöber's method. SiO_2 particles were prepared using TEOS in basic conditions. The particles diameter varied from ~ 30.6 nm, 66.8 nm, 213.8 nm It was then allowed to react with magnesium and carbon at 600 °C when SiC particles of 51.3 nm, 92.8 nm and 278.3 nm diameters were obtained. The product was purified with HCl to remove impurities like MgO. Absorption band at ~ 830 cm^{-1} confirms the presence of Si-C bond. It was further confirmed by other characterization techniques e.g. XRD and XPS [78]. A schematic of the sol-gel method is shown in fig. 1.

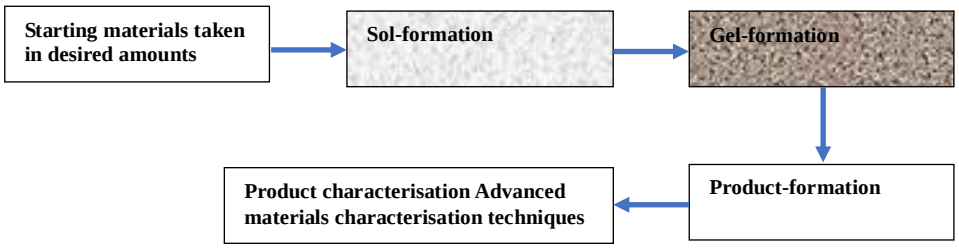


Fig. 1 Schematic showing SiC synthesis via sol-gel route.

3. Mechanical activation method: Numerous methods are devised to synthesize SiC, for example, carbothermal reduction, gas-phase reaction method and self-propagation high-temperature synthesis (SHS). Among these three SHS method can be carried out at a lower temperature than other methods and hence, it is a cost effective and environmentally friendly method. Also, the product obtained was of high-purity. Although, SHS method also required a temperature of 1327 °C to 1427 °C i.e. energy was required to bring about the reaction. Much research has been done to provide the additional energy from adding chemical promoters, microwaves, or preheating treatment. Li et al. used mechanical activation as one of the mean to facilitate the reaction. Silicon, carbon black and ammonium chloride (used as milling promoter) was ball-milled in a stainless-steel vessel for a maximum of 16 hours in air. The resultant mixture was then ignited in a graphite boat by titanium powder. XRD data shows that the mechanical activation helped to carry out the reaction only when the initial reaction mixture was ball-milled for more than 4 hours. Studies of the samples using advanced materials characterization techniques showed that this is a promising method to prepare ultrafine SiC at low temperature and in a cost-effective method in large scales [79].

Moskovskikh et al. also used mechanical activation technique to prepare SiC nanopowder and used high energy ball milling (HEBM). They used high-energy ball milling to powder the starting materials viz. silicon and graphite. This process increased the exposed surface area and hence increased the contact surface area. In the literature it was believed that HEBM: (i) decreases the self-ignition temperature of various combustible systems; (ii) expands their flammability limits; (iii) favours a more complete reaction, and (iv) increases the combustion

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

wave front velocity. The powder obtained in this way was pressed to pellets and was heated in stainless steel combustion chamber under argon. SiC in submicron size of high purity was formed. The effect of HEBM has significant effect on the combustibility of the Si/C mixture. The process of the combustion synthesis was feasible only after a threshold duration of milling was achieved (fig. 2) [80].

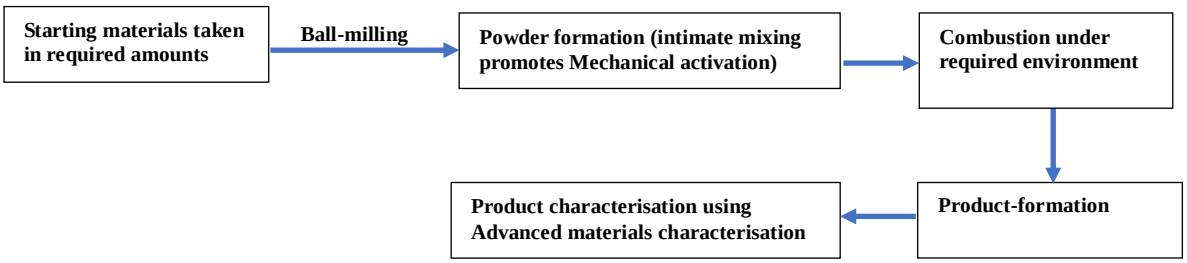


Fig. 2 Schematic showing SiC synthesis via mechanical activation.

Using low pressure plasma reactor: Plasma consists of partially ionized gas containing ions, electrons, atoms, and molecules and is considered as fourth state of matter. Extremely hot energetic electrons are present in cold plasma whereas rest of the molecules exist at much lower energy state. The hot energetic electrons can be used as source of energy to bring about a reaction [81]. McFarland et al. used a plasma reactor for the production SiC nanopowder. Large scale production of SiC nano-particles (diameter less than 10 nm) is challenging since normally these particles are made at higher temperature leading to agglomeration of particles. Silicon carbide nanoparticles with sizes of less than 10 nm have been produced. XRD results confirmed that the product was amorphous [82].

Plasma-dynamic method was used by Sivkov et al. an electro-discharge plasma jet generated by a high-current pulsed coaxial magneto-plasma accelerator was used. Results confirmed the presence of β-SiC. Some unreacted precursors were also present in the final product. It was observed that SiC content and particles sizes increase with increasing the energy level [83].

Using natural products: Nature has produced wonderful structures that can be used as templates for scientific invention. Several such biomineralization has been done, for example, wood was converted into alumina. Similarly, Dickon et al. used bamboo leaves as guide to synthesise SiC nanowires. Freshly cut bamboo were washed with water and pyrolyzed in argon atmosphere at 1100 °C to produce charcoal bio-templates. It was then soaked in Tetraethoxysilane (TEOS) for 5 to 7 days followed by heating at 1200–1500 °C for different durations ranging from 1 to 10 h. SiO_2 and SiC nanowires were formed. EDS analysis showed the existence of impurities like calcium on the tip of SiO_2 nanowires whereas iron was found on the tips of SiC nanowires (fig. 3). The authors believed that these impurities played an important role in the formation of nanowires [84].

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

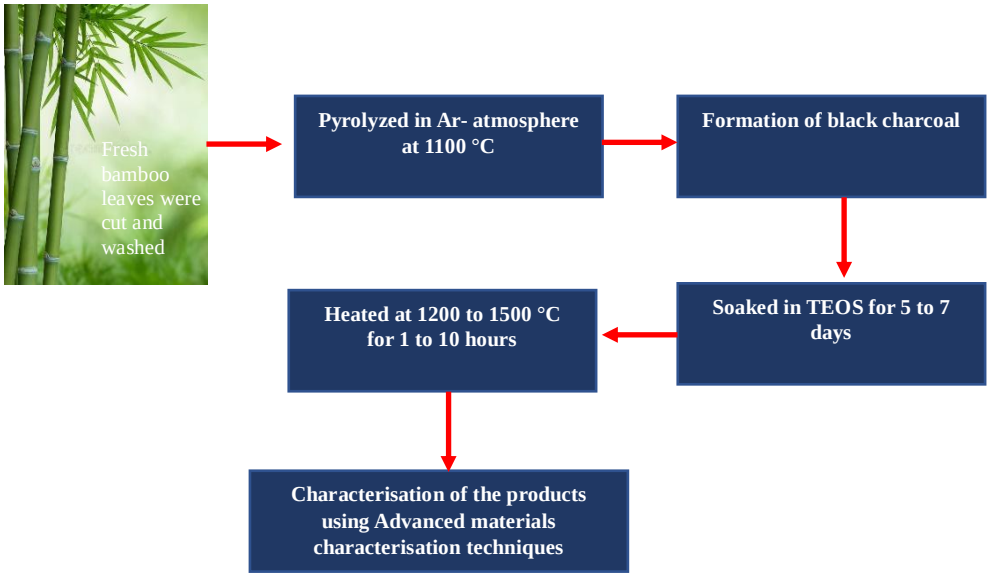


Fig. 3 Synthesis of SiC using palm leaves.

Carbothermal method was used to synthesize 6H-SiC (6H-SiC is a prototype of SiC, sec. 1.2) using bamboo leaves which was infiltered with TEOS above 1300 °C. Bamboo leaves were source of carbon and template for growth of SiC. TEOS was used as source of silicon. Fresh bamboo leaves were washed, cleaned, and soaked in TEOS for one day. The water of leaves hydrolyzes TEOS and convert them from hydrophobic to hydrophilic. The bamboo leaves after infiltration, were dried in air and then sintered in argon atmosphere in tube furnace for 1 h to 6 h at 1200-1400 °C. XRD analysis of the final samples have shown that SiC has hexagonal 6H- structure, while SEM images has confirmed their diameter of 60 nm to 160 nm range. The nanowires yield at top was found to be more as compared to the bottom of bamboo leaves. Cubic 3C-SiC structures were reported in the branched and nodes of bamboo like nanowires. It was believed that the high yield of the nanowires on the top surface was due to its hydrophilic property and low aluminum content. It was observed that morphology of the leaf surface affected the yield and the structure of SiC [85]. Hashim et al. developed a green method of synthesis of SiC nanowhiskers. Palm kernel shell (PKS) was used as source of carbon whereas silica was used as source of silicon. PKS, silica and liquid ethanol were mixed homogenously using ultrasonic bath for 2 hours. It was then dried to remove ethanol. The dried mixture was then pressed to form pellets. It was then exposed to microwaves (ChangSha Syno-Therm Co. Ltd., MW-L0316V). It was heated to 1400 °C at the rate of 30 ºC/min for 40 minutes. The pellet was allowed to cool down to room temperature inside the microwave cavity SiC nanowhiskers were successfully synthesized. Authors explained the growth of particles using vapor-liquid-solid (VLS) growth mechanism [86].

Microwave assisted synthesis of SiC: Acheson was the first to synthesize SiC at high temperatures (~ 2000 °C) [87]. This is a time-consuming process and reaction requires a very high temperature. Recently, microwaves have been used in chemical synthesis in laboratories as well as industries to make the heating process fast, simple, cost-effective, and environmentally friendly. The observed effective fast generation of heat inside the material is attributed to the microwave heating mechanism. Microwaves interact with the

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

atoms/ions/molecules of materials to generate heat inside the body. The microwave heating mechanism is understood by three mechanisms, namely (i) dipolar polarization (ii) conduction (iii) interfacial polarization and (iv) generation of Ohmic heating in metals through Skin-effect. The heat generated in molecules having permanent dipoles e.g. water is explained by dipolar polarization mechanism whereas the heating effect produced in conducting materials e.g. graphite is explained by conduction mechanism (fig. 4). Interfacial polarization is explained by a combination of dipolar polarization and conduction mechanism. Electric arcing can be observed when metal/metalloids are exposed to microwaves (fig. 6). In conventional heating heat energy is transferred from Microwave heating mechanism is discussed in detail by the authors as well elsewhere [88-97]. Whereas, in conventional heating method, when the work-piece is heated, initially, only the outside or the exposed part of the body is heated. Heat-energy is then transferred to internal layers via either conduction, convection or radiation mechanism (fig. 7). Though, the conventional heating mechanism is normally explained by a mixture all the three mechanisms. The heating rate is very much dependent upon the physical characteristics work-piece (fig. 5). These are mainly (i) specific heat (ii) thermal conductivity and (iii) density. Three characteristics of a material, combined, is called thermal diffusivity of a material.

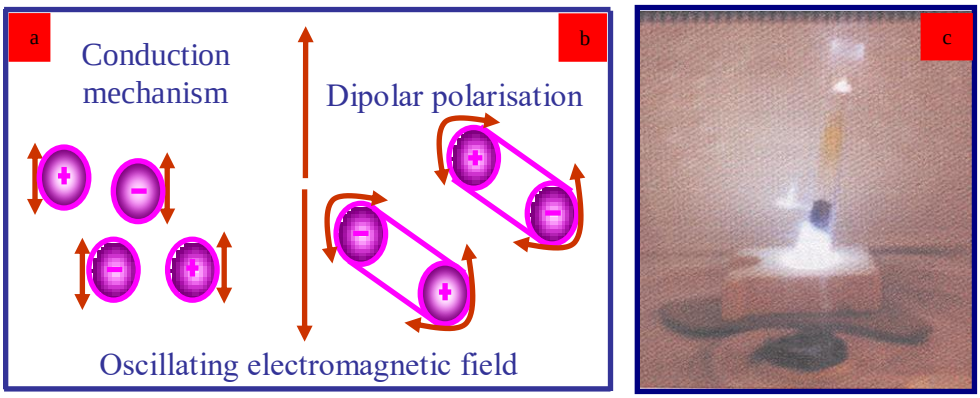


Fig. 4 Depiction of microwave heating [96]
a) Conduction mechanism
b) Dipolar polarisation
c) Photograph of electric arcing produced when As-S mixture was exposed to microwaves (a demonstration of Ohmic heating on microwave exposure)

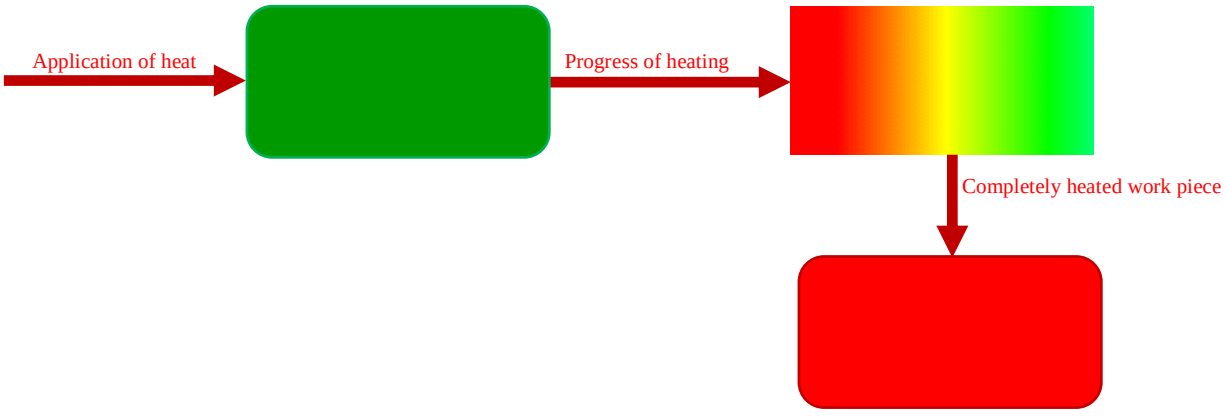


Fig. 5 Depiction of conventional heating mechanism

Microwaves are used successfully to prepare SiC in laboratories. Rad et al. used silica-gel and graphite powder as starting materials for the preparation of SiC. These were dispersed in

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

water and then dried to powder followed by palletization. β-SiC was formed in 60 minutes when these pellets were exposed to microwave for 60 minutes in a microwave oven working at 2.45 GHz and 900 W. Whereas it required 105 minutes of heating at 1500 °C in an electric furnace. Microwave heating provides a faster route of synthesis [98]. Multiwalled carbon nanotubes were used as starting materials. They were mixed together in liquid ethanol medium using an ultra-sonicator. The mixture was dried to powder and pelletized. It was then exposed to microwave oven of multimode cavity working at 2.45 GHz for 5 minutes. β-SiC was formed [99]. Kahar et al. also successfully synthesized SiC from silica and graphite via microwave heating in a multimode cavity reactor working at 2.45 GHz. It was reported that best result was obtained when the ratio of silica and graphite was taken as 1:3. Homogenization of powders were done by ultrasonication in a liquid medium. Ethanol was taken for this purpose [100]. Li et al. used rice husk to synthesize SiC to make the process cost-effective. Rice husk (RH) was carburized by a series of processing steps e.g. ball-milling and heating. It was then exposed to microwaves when nanostructured β-SiC particles were obtained in a 2.45 GHz microwave field in an argon atmosphere [101].

Several research groups used MW heating for the preparation of SiC with few limitations such as (i) reactant were heated in gas-environment; (ii) products contained impurities. To solve these problems and to make the overall process even more efficient than the previous methods Gregory et al. developed a different method of synthesis of SiC. Two sets of experiments were performed. In one of the sets of experiments, silicon and activated carbon were ball milled to produce a homogenous mixture whereas in another experiments silica and activated carbon were ball milled. These were pelletized using two different methods (i) pellets made of dry powder and (ii) pellets made from thick slurry of balled milled powders and distilled water. These were then exposed to microwaves (while keeping the pellets embedded in graphite) in an oven of multimode cavity (working at 2.45 GHz and 800 W magnetron). In another experiment a single mode cavity reactor was used as source of microwaves. β-SiC was prepared in a very short period (20 minutes to 5 seconds). Results showed that graphite can be used successfully as source of carbon while using single mode cavity reactor. The time of synthesis also reduced significantly (least ten-fold from the fastest reactions in the multimode cavity). Potentially the behaviour of different polymorphs of SiC can be controlled by using this method [102].

Synthesis of B_4C: The above discussed applications of silicon carbide and boron carbide shows that the synthesis of these compounds is utmost important. Several research groups have synthesised these. The routes of synthesis of these SiC and B_4C are discussed in the following sections.

Carbothermal reduction: Boron carbide was synthesized by carbothermic reduction using boric acid and petroleum coke. Coke was used as reducing agents. Mixture of boric acid and coke was ball milled and pressed (1000 kPa) to form pellets (20 mm diameter and 5 mm thickness). These specimens were heated up to 1400-1550 ^{o}C in a tube furnace with heating rate of 100^{0}C/min for 1-5 hour and cooled to room temperature at the rate of 5 °C/min under argon atmosphere. The powder obtained was washed with hot water to remove unreacted B_2O_3 followed by washing with acid and alkali to remove metallic impurities and reacted oxide. This is a cost-effective method. The samples contained less than 1 weight percent of free carbon [103].

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

In another attempt, boric acid and citric acid were used as source of boron and carbon respectively. Powders were dissolved in distilled water in molar ratio of 12:7 followed by heating for 3 hr at 100 °C in an oven. The gel was crushed into powder form for pyrolysis study. XRD results confirmed the formation of boron carbide. Agglomeration of particles were observed in electron microscopy (both TEM and SEM) [104].

A modified carbothermal reduction was also used for this purpose. Boric acid and carbon were used as starting materials. These were mixed and dried in oven for 24 h at 60 °C. The resultant product was pressed into green pellets followed by heat treatment in furnace between 500 and 2100 °C in argon flow. The furnace was then cooled to room temperature and final product was thus obtained [105].

$B_{13}C_2$ phase is most energetically favoured under-stoichiometric polytype. It can be prepared by sintering amorphous boron and carbon black mixture at 1900 °C. Its films can be synthesized by chemical vapor deposition from low-pressure $BCl_3/CH_4/H_2$/argon mixtures at the temperature ranging 1000 to 1400 °C. $B_{13}C_2$ nanowires were grown from $C/B/B_2O_3$ powder precursors at 1650 °C. The requirement of high temperature is the main disadvantage of these synthesis methods. Moreover, studies showed that $B_{13}C_2$ is metastable. To overcome all these obstacles, a fast pyrolysis self-propagating high temperature (SHS) synthetic route was used for preparing ultrafine powders of high purity single phase boron carbide $B_{13}C_2$. Appropriate amount of boron oxide, magnesium powder and sucrose were mixed in blender for one hour. The resultant mixture was pressed to cylindrical shape using hydraulic press. The cylinder was combusted in SHS reactor and then cooled to room temperature when a black powder was obtained. This (the crude black powder) was then washed with a mixture of concentrated hydrochloric acid, solution mixture of H_2O_2, HNO_3 and distilled water to remove impurities and by-products like MgO. The pH of this mixture was maintained to 7. This was followed by drying of the purified product for 24 hours at 80°C in a vacuum oven. Finally, grey powder was obtained. The XRD pattern shows pure phase of rhombohedral structure. Particle diameter in the range of 50 nm to 200 nm (average size = 90 nm) were obtained as observed under Field emission scanning electron microscope (FESEM) and Transmission electron microscope (TEM). This value of particle diameter (~ 88 nm) was further supported by calculated value obtained by Debye Scherrer equation. The possible reaction mechanism as reported by authors is as follows:

(i) Magnesiothermal reduction: This is a highly exothermic reaction and perhaps the following reaction takes place:
$C_{12}H_{22}O_{11} + 39B_2O_3 + 117Mg \rightarrow 6B_{13}C_2 + 117MgO + 11H_2O\uparrow$
(ii) Carbothermal reduction: This is highly endothermic step of the reaction
$43C_{12}H_{22}O_{11} + 156B_2O_3 \rightarrow 24B_{13}C_2 + 473H_2O\uparrow + 468CO\uparrow$
Hence, this process can be regulated by properly adjusting the reactant ratio [106].

Powder B_4C was synthesized by pyrolysis of the gel formed from boric acid and polyvinyl alcohol followed by carbothermal reduction. The gel was dried followed by pyrolysis in argon flow at 600 °C for 2 h. The resultant mixture was heated in a graphite crucible at 1200-1500 °C in argon flow for 3 h to bring about carbothermal reduction. XRD results confirmed the formation of B_4C. Morphology of B_4C particles were dependent upon the amount of glycerine added. Morphology and amounts of residual carbon was dependent upon the amount of glycerine added to the precursor mixture. Regularly shaped particles as well as less residual carbon were obtained when the amount of glycerine was increased [107]

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Low temperature synthesis: Several methods were employed to synthesize boron carbide. The two major problems are (i) presence of residual carbon and (ii) requirement of high temperatures for synthesis. To solve these problems and to synthesize boric carbide at a low-temperature, polyvinyl borate (PVBO) precursor was prepared by condensation of polyvinyl alcohol and boric acid. The precursor of PVBO was pyrolyzed in air for 2 hours at 450-700°C. It was then powdered and heated under argon flow for 5 hours at 1100-1300 ^{0}C. The product was studied using XRD which confirmed the formation of B_4C [108].

Powder B_4C can be prepared by carbothermal reduction of B_2O_3. The limitations of powder technology are (i) shaping of the powder and (ii) requirement of high-temperatures. To avoid the problems of powder technology efforts are made to use polymers as one of the starting materials for the preparation of B_4C at low temperatures. Boric acid was used as source of boron and polyvinyl alcohol (PVA) was used as source of carbon. Separate solutions of boric acid and PVA were made in distilled water and then mixed together in hot condition. This resulted in the formation of white and rubbery product. It was then collected in petridish and dried. The dried product was crushed when a white powder was obtained. The precursor compound was pyrolyzed in air at 400°C and 800°C for 3 hours to get final product. X-ray diffraction (XRD) showed that boron carbide (B_4C) having orthorhombic crystal structure was formed (fig. 6). The result was further supported by Fourier Transform Infrared spectroscopy (FTIR) analysis. Two samples (pyrolyzed at 400°C and 800°C) were studied. The absorption band obtained at 1190 cm^{-1} confirms the presence of B-C bond showing that boron carbide was formed. The other absorption bands observed were O-H stretching vibration at 3200 cm^{-1} and B-O stretching vibration at 1450 cm^{-1} [109].

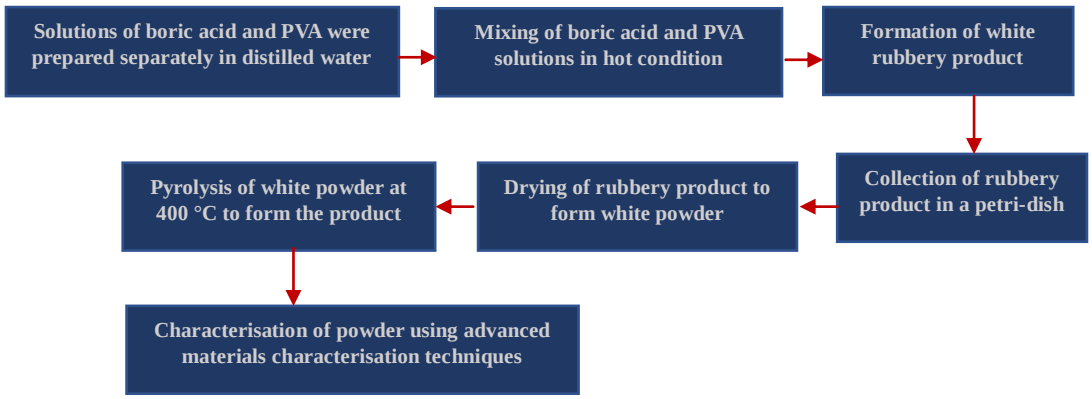


Fig. 6 Schematic of low temperature synthesis of B_4C.

To further simplify the process and to solve the above stated problems Kobayashi et al. devised a new synthetic route. In this method condensed boric acid-glycerin product was used. Equimolar mixture of boric acid and glycerin were mixed and dehydrated at 150 °C to form the condensed product. The resultant product was heated in air for 2 h at 250 °C followed by pyrolysis in air for 2 hours at 450 – 650 °C. Carbon was removed to form the precursor powder. It (precursor powder) was powdered using an agate mortar and pestle. It was then heated at 1100–1300 °C for 5 h in the flow of argon (200 ml/min) at a heating rate of 10 °C/min [110].

Li et al. developed a cost-effective route of synthesis of boron carbide at a low-temperature with a small amount of free carbon. Poly(resorcinol borate) (PRB) with an aromatic structure and high char yield was chosen as the aromatic polymeric precursor. The results indicate that

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

the rod-like structure of crystalline B_4C is successfully synthesized at 600 °C, and the free carbon can be reduced to about 0.8 wt% in the final product [111]

Microwave assisted synthesis of B_4C: As discussed above application of microwaves fastens the rate of heating, several research groups used this heating methodology for the preparation of B_4C. The boron powder obtained from electrodeposition in house was used as source of boron, carbon black as source of carbide and PVA or stearic acid as binder. The boron powder, carbon black and binder were ball milled for 1 h. In another set of experiment, magnesium (~1%) and another component were ball milled. The ball milled samples were converted into disc shaped compacts of 25 mm diameter and 5 mm thick using die and plunger made of graphite. The compacts were embedded in carbon black in an alumina crucible. The crucible was then placed in another alumina crucible filled with SiC (susceptor material). It was then exposed to microwaves (2.45 GHz, 1200 Watt). B_4C and B_8C were formed. The samples formed from MW heating showed B-C absorption bands at ~1190 cm^{-1} [112].

Carbide of boron was synthesised using microwave assisted carbothermal reduction. High purity disordered carbon black and boric acids were used as source of carbon and boron. Different ratios boric acid and carbon black were added to ethanol in different sets of experiments with an aim to synthesise carbide of boron with different percentage of boron. The mixture was then heated at 50°C to partially evaporate the solvent form a paste like mixture. The paste was then extruded and heated at 50°C in a kiln. Samples were exposed to microwaves for 20 minutes in a domestic oven (2.45 GHz, Cober, USA). The DMO cavity was flushed with argon (rate of flow of argon = 1 liter/min) before the experiment. Crystals of boron carbide in nanometer scale were formed. The reaction did not require any catalyst e.g. cobalt (fig. 7). Microwave carbothermal reduction process is fast, cost-effective and environmentally friendly [113].

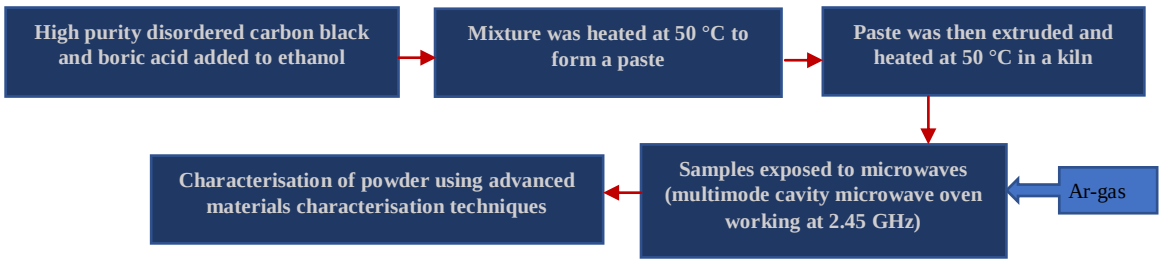


Fig. 7 Schematic showing microwave assisted synthesis of B_4C.

Boron methoxide, boron ethoxide, and boron tri-isopropoxide and bi-glycerol borate were used as source of boron whereas carbon black, calcined saccharose and saccharose were used as source of carbon. A sol-gel method was used for this purpose. It was observed that the rate of reaction was considerably faster in microwave assisted synthesis than the conventional heating method which can be attribute to the microwave heating mechanism [114]

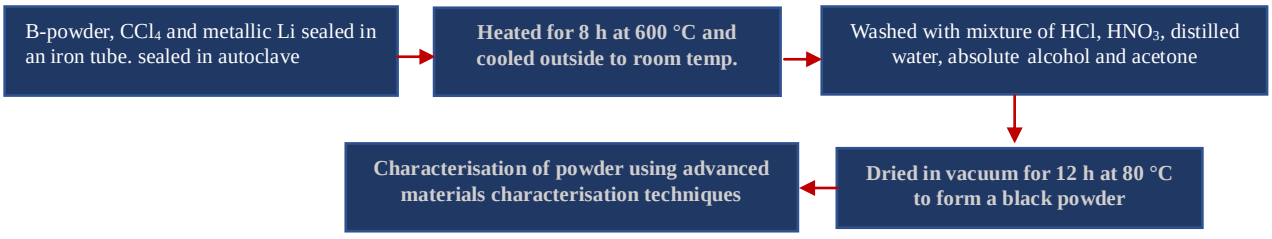
Use of natural products as precursors: A homogenous gel was prepared using boric acid and sucrose melt. It was then isothermally heated when black coloured dry xerogel was formed. This was then pyrolysed under the flow of ultra-high pure argon at 1000 °C for 2 hours, crushed and pressed using hydraulic press to form pellets. Pellets were heated in a graphite boat at high temperatures (ranging from 1300 to 1550 °C). FTIR absorption band at 1015 cm^{-1} shows the presence of B-O-C bond suggesting that boric acid and sucrose formed a complex during gelation. Though the sample obtained after pyrolysis did not show this absorption

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

band showing that this bond broke at high temperatures. Formation of B_4C was confirmed from XRD data. The particles size varied from 0.1 µm to 100 µm as observed under TEM [115]. Nanocrystalline boron carbide was prepared from boric acid and sucrose-gel as precursors. Stoichiometric amount of boric acid, sucrose, phenolphthalein, sodium hydroxide and D-mannitol were mixed in a stainless steel-vessel and heated in a controlled environment when boron carbide was formed. The beauty of this synthetic route lies in the use of a cheap material like sucrose as source of carbon. It was also observed that the percentage of free carbon in the final product was 3% less than the boron carbide synthesized using other routes of synthesis [116]. Cihangir et al. used boric acid as source of boron and sugar as source of carbon. These starting materials were taken in calculated amounts so that boron to carbon ratio should be 1:1. Sugar was heated until it became black. It was then ball milled. These materials were then heated to high temperatures in separate set of experiments. XRD results suggested that B-C bond was formed between 1400 °C to 1600 °C. However, FTIR results showed bands at 1190 cm^{-1} and 1450 cm^{-1} suggested the formation boron carbon bond. It was also evident from FTIR results that boron carbon bond started forming 400 °C. The existence of the B-O bands at 1400 °C suggests the presence of oxygen in the sample even though it is not visible XRD pattern. Studies showed that at higher temperatures ordering and crystallization in the structure occurs [117].

Boron carbide was synthesized by low temperature technique. Boric acid was used as source of boron and sucrose, potato starch, phenol-formaldehyde resin, and carbon black as source of carbon. A reference material was obtained by mixing boric acid with carbon black. X-ray diffraction pattern showed the formation of B_4C. The particles were rhombohedral as observed under SEM. The XRD pattern of sample heat treated at 1350 °C shows presence of amorphous carbon and boron anhydride which confirms the onset of boron carbide synthesis. When temperature of heat treatment raises to 1450 °C, higher boron carbide contents were found in the sample. For sample, heat treated at 1550 °C, rhombohedral crystalline structure of the boron carbide was reported, but, when boron was not used in excess in premixes then product obtained shows disordered carbon as the main component. Sample synthesized using sucrose and excess boric acid, shows presence of coarse needle shaped crystals. Premix in which boric acid content was reduced and sample was processed, single isometric crystals of boron carbide was seen in SEM image [118].

Solvothermal reduction: Nanocrystalline B_4C *via* solvothermal reduction. Carbon tetrachloride (CCl_4), amorphous boron and metallic lithium were used as starting materials. These were kept in an iron tube and sealed in under argon atmosphere in an stainless steel autoclave. The autoclave was heated for 8 hours at 600 °C. The product obtained inside the iron tube was washed with hydrochloric acid, nitric acid, distilled water, absolute alcohol, and acetone to remove lithium chloride, carbon, and other impurities. It was then dried under vacuum at 80 °C for 12 h. XRD results showed hexagonal B_4C phase with lattice constants a = 5.606 and c = 12.089. Transmission electron microscopy suggested the formation of agglomerates (fig. 8) [119].



ISSN: 0971-1260
Vol-22-Issue-16-August-2019

Fig. 8 Schematic showing synthesis of B_4C via solvothermal reduction.

Sol-gel method: Carbide of boron was synthesized by sol-gel method. Boric acid and Citric acid were used as source of boron and carbon. This research presents that, for minimizing the free carbon in production excess acid boric must be used. The ratio of raw materials for compensation of boron loss, was less than as reported in literature. Homogenous mixing of reactants in sol-gel process was more than the conventional mixing; showing that the intimate mixing of reactants affects kinetics of reaction significantly. It was also observed that the temperature played an important role. B_4C nanoparticle of narrow size distribution was formed [120].

Solid state synthesis: Suri et al. made efforts to prepare boron carbide through solid-state synthetic routes starting from elemental boron as well as elemental carbon. Boron powder was prepared by fused salt electrolysis route. Petroleum coke was used as source of carbon. The powdered elements were pressed to form a pellet. The pellets were then heated in a graphite crucible. The temperature was kept between 1500 °C to 1900 °C. It was concluded that it is challenging to synthesize carbon free boron carbide powder. B_8C was formed when the amount of boron was increased. Carbides of boron and free carbon were at equilibrium with each other. Properties investigated using advanced materials characterization techniques matched with the reported value [121].

Bombardment by boron ion: Thin films of ~ 100 nm to 500 nm fullerene was deposited on silicon wafers by resistance heating at 700 °C under vacuum. It was then irradiated with single and triple charged boron ions (B^+, B^{3+}). The applied energies were 15 and 45 keV. The identification of B–C bonds in irradiated films indicates the formation of amorphous boron carbide [122].

Synthesis of B_4C using polymer precursor: In another effort Rahimnejad et al. prepared boron carbide using boric acid and polyvinyl alcohol. The precursor gel was prepared using the above stated starting materials which was then pyrolyzed followed by heat treatment. Boron carbide was formed at ~1600 °C under argon. Authors claimed the formation of carbon free boron carbide [123].

Electrospinning route: Aqueous mixture of polyvinyl alcohol (PVA) and boric acid (BA) were prepared. Viscosity and pH were optimized. It was then electro-spun to form fibers. Fibers were calcified at 500 °C. XRD results confirmed the formation of boron carbide [124].

Spray Pyrolysis: Ozcelik *et al.* also used sucrose as source of carbon while using spray pyrolysis route. Solutions of these components were heated for several hours under argon flow. In a different set of experiment nickel was used as catalyst. Boron carbide nanoparticles were formed. Addition of nickel did not show any obvious effect. Fig. 9 shows the schematic of the experimental set-up as depicted in the original article [125].

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

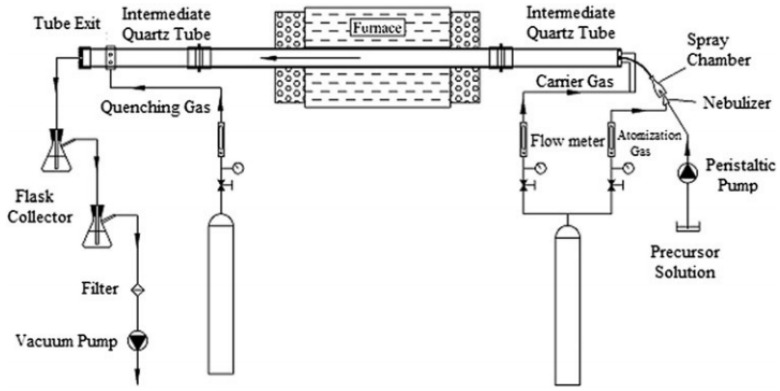


Fig. 9: Schemtic of the experimental set-up used for synthesis of boron carbide as depicted by authors in the original literature. Permission is taken from the journal for incorporating the figure here.

Summary: SiC and B_4C have a wide range of application because of their unique properties. For example, they can be used in the preparation of various types of composites because they exhibit incomparable mechanical properties. They are used as biomaterials because of their chemical inertness and can be used in power electronic applications as they have wonderful semiconducting properties. They also be used as catalysts in laboratories and industries, for bioimaging, as hydrophobic coating and in nuclear sectors. There is an utmost need to prepare these materials with exceptional purity. Several methods have been used for the preparation e.g. carbothermal reduction, solvothermal reduction, via mechanical activation, sol-gel method, low-temperature synthesis, using natural products, electrospinning and using microwaves, to name a few. Further work can be done to improve the methods of preparation of these materials so that the novel method that should be fast, simple, cost-effective and environmentally friendly and that can produce purer material than the existing ones. A theoretical investigation of these materials will lead to a better understanding of the area which may prove that the scope of applicability of these materials are even wider than the current knowledge says

References:

1. http://periodictable.com/Properties/A/AtomicRadius.v.html, Last accessed: 7 July 2018

2. https://periodictable.me/electronegativity-chart/, Last accessed: 7 July 2018

3. Cotton, F.; Wilkinson, G.; Murillo, C. A.; Bochmann, M.; Advanced Inorganic Chemistry, 6th Edition, ISBN: 978-0-471-19957-1, Chapter 7, pp. 221

4. Wu, R.; Zhou; Yue, C., Y.; J., Wei; Pan, Y. *Prog. in Mater. Sci.*, **2015**, *72*, 1–60

5. http://accuratus.com/silicar.html, Last accessed 28/6/2018

6. Zhu, D.; Gao, S.; Zhang, C.; Wu, H. Y.; Pan, Y.; Liu, Y. F. *J. Mater. Sci.*, **2012**, *47*, *492*, 1–7

7. Perisanu, S.; Gouttenoire, V.; Vincent, P.; Ayari, A.; Choueib, M.; Bechelany *Phys. Rev. B.*, **2008,** *77*, 4–12

8. Seong, H. K.; Choi, H. J.; Lee, S. K.; Li, J. I.; Choi, D. J. *Appl. Phys. Lett.*, **2004**, *85*, 256–8

9. Li, Y. B.; Dorozhkin, P. S.; Bando Y.; Golberg, D. *Adv Mater.* **2005,** *17*, 545–9

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

10. Cui, H.; Zhou, J.; Yang, G. Z.; Suna, Y.; Wang, C. X. *Cryst Eng Comm*, **2011**,*13*, 902–6

11. Shim, H.; Huang, H. C. *Nanotech.*, **2007,***18,* 1-5

12. Papanikolaou, N.; *J. Phys. Condens. Matter.*, **2008**, *20*, 1–6

13. Rusheng, W.; Sheng, S.; Kun Y.; Yingxin, C.; Yan P. *J. Appl. Phys.*, **2013,** *113,* 053503-4

14. Zhang, Y. F.; Huang, H. C. *Comput. Mater. Sci.*, **2008,** *43*, 664–9

15. Shim, H. W.; Kuppers, J. D.; Huang H. C. *J. Nanosci. Nanotechnol.*, **2008**, *8*, 3999–4002

16. Kohno, H.; Mori, Y.; Takeda, S.; Ohno, Y.; Yonenaga, I.; Ichikawa, S. *Appl. Phys. Express.* **2010**, 055001–3

17. https://en.wikipedia.org/wiki/Wetting, Last accessed 7 July 2018

18. Niu, J. J.; Wang, J. N.; Xu, Q. F. *Langmuir*, **2008**, *24*, 6918–23

19. Niu, J. J; Wang, J. N. *J Phys Chem B*, **2009**, *113*, 2909–12

20. Kwak, G.; Lee, M.; Senthil, K.; Yong, K. *Langmuir*, **2010,** *26*, 12273–7

21. Yana, C.; Lifeng, W.; Jianyuea, R. *Chi. J. of Aero.*, **2008**, *21*, 578-584

22. Cheng, G.; Chang, T.; Qin, Q.; Huang, H.; Zhu, Y. *Nano Lett.* **2014**, 14, 754−758

23. Bazzar, M.; Ghaemy, *M. Compos. Sci. Technol.*, **2013**, *86*, 101–8

24. Akbarpour, M. R.; Salahi, E.; Hesari, F. A.; Yoon, E. Y., Kim, H. S.; Simchi, A. *Mater Sci Eng A*, **2013**, *568*, 33–9

25. https://www.ube.com/contents/en/chemical/continuous_inorganic_fiber/, Last accessed 7 July 2018

26. Yang, W.; Araki, H.; Tang, C. C.; Thaveethavorn, S.; Kohyama, A.; Suzuki, H. *Adv. Mater.*, **2005**,*17*, 1519–23

27. Chu.; Y. H.; Fu, Q. G.; Li, H, J.; Shi, X. H.; Li, K. Z.; Wen, X.; Shang, G. N. *J. Am. Ceram. Soc.*, **2012**, *95*, 739–45

28. https://technology.nasa.gov//t2media/tops/pdf/LEW-TOPS-25.pdf, Last accessed: 7 July 2018

29. https://www.britannica.com/science/field-emission, Last accessed: 7 July 2018

30. https://www.britannica.com/science/electronic-work-function, Last accessed: 7 July 2018

31. Linyue, L.; Liu, A.; Song, B.; Ling, L.; Peng, J.; Xiaoping, O. *Sci. Repo.*, **2017**, 7, 13376

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

32. http://srmsc.org/pdf/004430p0.pdf, Last accessed: 7 July 2018

33. http://www.alternatewars.com/WW3/WW3_Documents/ABM_Bell/ABM_Ch8.htm, Last accessed: 7 July 2018

34. Toftul, A. *Thesis 'Presented to the Faculty of The Graduate College at the University of Nebraska, Lincolon, In the partial fulfilment of requirements for the Degree of Master of Science in Electrical Engineering*, **2014, 1-2**

35. Runhua, H; Yonghong, T.; Ling, W.; Gang, C.; Song, B.; Rui, L.; Yun, L.; Zhifei, Z. *J. of Semicon.*, **2016**, *37*, 084001-4

36. Gary, W.; Hunter, P.; Neudeck, G.; Chen, L.; Knight, D.; Liu, C.; Wu; Q. *NASA Tech. Memo.*, **113159**

37. Liu, H. L.; She, G. W.; Mu, L. X.; Shi, W. S. *Mater. Res. Bull.*, **2012**, *47*, 917–20

38. Hao, J. Y.; Wang, Y. Y; Tong, X. L.; Jin, G. Q.; Guo, X. Y. *Int. J. Hydro. Ener.*, **2012**, *37*, 15038–44

39. He, C.; Wu, X.; Shen, J.; Chu, P. K. *Nano. Lett.*, **2012**, *12*, 1545−1548

40. Zhou, W., Lijun, Y.; Ying, W., Yafei, Z. *Appl. Phys. Lett.*, **2006**, *89*, 013105

41. Chiu, S. C.; Yu, H. C.; Li, Y. Y. *J. Phys. Chem.*, **2010**, *14*, 1947–52

42. Beke, D.; Szekrényes, Z.; Pálfi, D.; Róna, G.; Balogh, I.; Maák, P. A.; Katona, G.; Czigány, Z.; Kamarás, K.; Rózsa, B.; Buday L., Vértessy, B.; Gali, M. *J. Mater. Res.*, **2012**, 1-5

43. Fan, J.; Li, H.; Jiang, J.; Leo, K. Y.; Yun S.; Lam, W.; Chu, P. K. 3C–SiC nanocrystals as Fluorescent Biological Labels; **2008**, *4*, 1058–1062

44. Beke, D.; Szekrényes, Z.; Czigány, Z.; Kamarás, K.; Gali, A. *Nanoscale*, **2015**, *7*, 10982–10988

45: Gerhardt, R. *InTech*, Properties and Applications of Silicon Carbide, **2011**, *ISBN: 978-953-307-201-2*, 276-297

46. Balakrishnarajan, M. M.; Pancharatna, P.; Hoffmann, R. *New J. Chem.*, **2007**, **31**, 473–485

47. Reddy, K. M.; Liu, P.; Hirata, A.; T. Fujita, T.; Chen, M. W. *Nat. Commn*, **2013**, *4:2483*, 1-5

48. Reddy, M. K.; Guo, J. J.; Shinoda, Y.; T. Fujita; Hirata, A.; J. P.; McCauley, J. W.; Chen, M.W. *Nat. Commns.*, **2012**, *3:1052*, 1-5

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

49. Shirvanimoghaddam, K.; Khayyam, H; Abdizadeh, H.; Karbalaei A. M.; Pakseresht, A. H.; Ghasali, E.; Naebe, M. *Mater. Sc. and Eng.: A*, **2016**, *658*, 135-149

50. Zeng, X.; Liu, W. *J. of Mater. Eng. and Perform.*, **2016**, *25*, 5014-5019

51. Mohanty, R. M.; Balasubramanian, K. S. *J. of Mat. Eng. and Perform.*, **2016**, *25*, 5014–5019

52. Miyazaki, K.; Hagio, T.; Kobayashi, K. J. of Mat. Sc., 1981, 16, 752–762

53. Busquets-Mataix, D.; Salvador, M. D. *A. J. of Compo. Mat.*, **2009**, 987-995

54. https://en.wikipedia.org/wiki/Tribology, Last accessed: 7 July 2018

55. Cafri, M.; Dilman, H.; Dariel, M., P.; Frage, N. *J. of the Eur. Ceram. Soc.*, **2012**, *32*, 3477–3483

56. Kommel, L.; Kimmari, E. *Mat. Sci.*, **2006**, *12*, 28-52

57. Chapman, T. R.; Niesz, D. E.; Fox R. T.; Fawcett T. *Wear*, **1999**, *236*, 81–87

58. Kovziridze, Z. D.; Mestvirishvili, Z.; Tabatadze, G.; Nizharadze, N. S.; Mshvildadze, M.; Nikoleishvili, E. *J. of Elec. Col. and Therm. Control*, **2013**, *3*, 43-48

59. Hu, D.; Küçer, R.; Küçer, N.; World Conference on Technology, Innovation and Entrepreneurship, Procedia - Social and Behavioral Sciences, **2015**, *195*, 1752 – 1756

60. https://www.nuclear-power.net/glossary/boron-10/, Last accessed: 7 July 2018

61. Subramanian, C.; Suri, A. K.; Murthy, T. S. R. Ch. Development of Boron-based materials for nuclear applications Materials Group, BARC News Letter, **2010**, 313

62. Domnich, S. R.; Richard, A. H.; Chhowalla, M. *J. Am. Ceram. Soc.*, **2011**, *94*, 3605–3628

63. https://en.wikipedia.org/wiki/Betavoltaic_device, Last accessed: 7 July 2018

64. Bao, Ruqiang, Thesis (Publication Number: AAT 3435861; ISBN: 9781124351155; Advisor: Chrisey, Douglas B) 'Presented at Rensselaer Polytechnic Institute The Graduate College, New York, for the partial fulfilment of requirements for the degree of Ph.D. in Electro, and Elec. Eng., Mat. Sc., **2010**, 1-3

65. Peter A. Dowben University of Nebraska-Lincoln, pdowben@unl.edu Anthony N. Caruso Lincoln, NE (US) Yaroslav B. Losovyj Louisiana State University at Baton Rouge, ylozovyy@indiana.edu, Patent NO.: US 6,774,013 B2, Date of Patent: Aug. 10,2004

66. Hwang, S. D.; Yang, K.; Dowben, P. A.; Ahmad, A. A.; Ianno, N. J.; Li, J. Z.; Lin, J. Y.; Jiang, H. X.; McIlroy, D. N. *Appl. Phys. Lett.*; **1997**, *70*, 1028-1030

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

67. Adenwalla, S.; Welsch, P.; Harken, A.; Brand, J. I.; Sezer, A.; Robertson, B. W. *App. Phys. Lett.*, **2001**, *79*, 4357-4359

68. Hwang, S. D.; Remmes, N. B.; Mcllroy, D. N.; Dowben, P. A. *J. Vac. Sci. Tech. B*, **1996**, *14*, 2957

69. McIlroy, D. N.; Hwang, S. D.; Yang, K.; Remes, N; Dowben, P. A.; Ahmad, A. A.; Ianno N. J.; Li, J. Z.; Lin, J. Y.; Jiang, H. X. *Appl. Phys. A: Mater. Sci. Process.*, **1998**, 67, 335

70. Hwang, S. D.; Remmes, N. B.; Dowben, P. A.; Mcllroy D. N. *J. Vac. Sci. Technol. B.*, **1996**, *14*, 2957-2960

71. Braunstein, G.; Muraviev, A.; Saxena, H.; Dhere, N.; Richter, V.; Kalish, R. *Appl. Phys. Lett.*, **2005**, 87, 192103

72. Hong, N.; Langell, M.; Liu, J.; Kizilkaya, O.; Adanwalla, S. *J. Appl. Phy.*, **2010**, *107*, 024513

73. Echeverria, E.; Dong, B.; Peterson, G.; Silva, J. P; Wilson, E. R.; Driver, M. S.; Jun, M. S.; Stucky, G. D.; Knight, S.; Hofmann, T.; Han, Z. K.; Shao, N.; Gao, Y.; Mei, W. N.; Nastasi, M.; Dowben, P. A.; Kelber, J. A. *J. Phys. D: Appl. Phys.*, **2016**, *49*, 355302,

74. https://en.wikipedia.org/wiki/Charge_transport_mechanisms, Last accessed 7 July 2018

75. Emin, D. *AIP Cof., Proc.*, **1991**, *231*, 65

76. Schmechel, R.; Werheit, H. J. *Solid State Chem.*, **1997**, *133*, 335-341

77. Najafi, A.; Golestani, F.; Rezaie, H. R.; Ehsani, N. *Pow. Tech.*, **2012**, *219*, 202–210

78. Dasog, M.; Larissa, F. S.; Purkait, T, K.; Veinot, J. G. C. *Chem. Commun.*, **2013**, *49*, 7004—7006

79. Yang, Y.; Lin, Z.; Li, J. T. *J. of the Eur. Ceram. Soc.*, **2009**, *29*, 175–180

80. Mukasyan, A. S.; Lin, Y. C.; Rogachev A. S.; Moskovskikh, D. O. *J. Am. Ceram. Soc.*, **2013**, *96*, 111–117

81. https://en.wikipedia.org/wiki/Plasma_(physics), Last accessed: 7 July 2018

82. Lin, H.; Gerbec, J. A.; Sushchikh M.; McFarland, E. W. *Nanotech.*, **2008**, *19*, 325601 (8pp)

83. Nikitin, D.; Sivkov, A. *IOP Conf. Series: Mater. Sc. and Eng.*, **2015**, *93*, 012039

84. Teresa, L. Y.; Dickon, H. L. Ng; *J. Am. Ceram. Soc.*, **2007**, *90*, 559–564

85. Zhu, J., Jia, J.; Kwong, Dickon H. L. Ng *Dia. & Related Mater.*, **2013**, *33*, 5–11

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

86. Voon, C. H.; Lim, B. Y.; Gopinath, S. C. B.; Tan, H. S., Tony, V. C. S.; Arshad, M. K.; Foo1, K. L.; Hashim, U. *IOP Conf. Ser.: Mater Sci. and Eng.*, **2016**, *160*, 012057

87. Guichelaar P.J. (1997) Acheson Process. In: Weimer A.W. (eds) Carbide, Nitride and Boride Materials Synthesis and Processing. Springer, Dordrecht

88. Meredith, R. Engineers' handbook of industrial microwave heating, Institution of Electrical Engineers, London **1998**

89. http://www.tan-delta.com/, last accessed: 7 July 2018

90. Galema, S. A.; Microwave chemistry, *Chem. Soc. Rev.*, **1997**, *27*, 233-238

91. Whittaker, A. G.; Mingos, D. M. P. *J. Chem. Soc. Dalton Trans.*, **1995**, 2073-2079

92. Whittaker, A.; Mingos, D.M.P. *J. Chem. Soc., Dalton Trans.*, **2002**, 3967-3970

93. Feynman, R.; Leighton, R.; Sands, M. The Feynman lectures on physics. Vol. 2, **1964**

94. Prasad, N.; Furniss, D.; Rowe, H.; Miller, C.; Gregory, D.; Seddon, A. J. Non-Cryst. Solids, **2010**, 356 (41-42), 2134-2145

95. Prasad, N.; Seddon, A. Proc. ICTON'10 (IEEE), **2010**, 1-4

96. Prasad, N.; Furniss, D.; Gregory, D.; Kingman, S. *Inter. Sym. on Non-Oxide and New Opt. Gla. (ISNOG)*, **2006**, IISc, Bangalore, India

97. Vats, S.; Sharma, R. Prasad, N. *J. of Chem. and Pharm Res.*, **2018**, *10*, 190-198

98. Ebadzadeh, T.; Marzban-Rad, E.; *Mater. Charac.*, **2009**, *60*, 69–72

99. Tony, V. C. S.; Voon, C. H.; Lee, C. C.; Lim, B. Y.; Arshad, M. K.; Gopinath, S. C. B.; Foo, K. L.; Ruslinda, A., R.; Hashim, U.; Nashaain, M. N. *Ceram. Inter*¸ **2016**, *42*, 17642-17649

100. Kahar, S. M.; Voon, C. H.; Lee, C. C.; Lim, B. Y.; Arshad, M. K.; Foo, K. L.; Liu, W. W.; Ruslinda, A. R.; Hashim, U.; Adelyn, P. Y. P.; Huda, A. R. N.; Lee, H. C.; Rahman W.; *IEEE-Explore*, **2015**, 1-4

101. Li, J.; Shirai, T.; Fuji, M.; Li, J. *Ad. Pow. Tech.*, **2013**, *24*, 838-843

102. Carassiti, L.; Jones, A.; Harrison, P.; Dobson, P. S.; Kingman, S.; MacLaren, I.; Gregory, D. H. *Energy Environ. Sci.*, **2011**, 4, 1503–1510

103. Alizadeha, A.; Taheri-Nassaj, E.; Ehsani, N. *J. of the Eur. Ceram. Soc.*, **2004**, 24, 3227–3234

104. Khanra, A. K. *Bull. Mater. Sci*., **2007**, *30*, 93–96

105. Jung, C. H.; Lee, M. J.; Kim; C. J. *Mater. Lett*, **2004**, *58*, 609 – 614

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

106. Zhang, L.; Gu, Wang, W.; Wang, J.; Zhao, G.; Qian, Q.; Zhang Z.; Zhang, F. *J. of the Cera. Soc. of Jap.*, **2011**, *119 (8)*, 631-634

107. Chen, X. W.; Dong, S. M.; Kan, Y. M.; Zhou, H. J.; Hu, J. B.; Ding, Y. S. *RSC Adv.*, **2016**, *6*, 9338–9343

108 Yanase, I.; Ogawara, R.; Kobayashi K. *Mater. Lett.*, **2009**, *63*, 91–93

109. Mondal, S.; Banthia, A. K. *J. of the Euro. Ceram. Soc.*, **2005**, 25, 287–291

110. Kakiage, M.; Tahara, N.; Yanase, I.; Kobayashi, H. *Mater. Let.*, **2011**, *65*, 1839–1841

111. Wang, S.; Li, Y.; Xing, X. *J. Mater. Res.*, **2018**, *33*, 1659-167

112. Harini, R. S.; Manikandan, E.; Anthonysamy, S.; Chandramouli, V.; Eswaramoorthy, D.; *AIP Conf. Proc. 1512*, **2013**, 1244

113. Gunnewiek, F. K. R.; Souto, P. M.; Kiminami, R. H. G. A. *J. of Nanomater*., **2017**, 3983468, 1-8

114. Rodríguez, M.; Ortiz, U.; Aguilar, J.; Valdez, Z. Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León Apartado Postal 076F, Cd. Universitaria, San Nicolás de los Garza, NL. 66450 México

115. Pilladi, T. R.; Ananthasivan, K.; Anthonysamy, S.; Ganesan, V. *J. Mater. Sci*., **2012**, *47*, 1710–1718

116. Pilladi, T. R.; Ananthansivan, K.; Anthonysamy, S. *Pow. Tech.*, **2013**, *S0032-5910(13)00359-8*, 1-27

117. Avcıata, O.; Ergun, C.; Erden, I.; Üstündağ, C.; Yılmaz, S.; Cihangir, S. *Global Roadmap for Ceramics-ICC2 Proceedings*, **2008**

118. Zakharova, K.; Mednikova, A.; Rumyantsev, V.; Genusova, T. *03AET09*, **2013**, *2*, 4 pp

119. Gu, Y.; Chen, L.; Qian, Y.; Zhang, W.; Ma, J. *J. Am. Ceram. Soc.*, **2005**, *88*, 225–227

120. Bigdeloo, J. A.; Hadian, A. M.; Abdizadeh, H.; Baharvandi, H. R. *ICRAMME 05*, **2005**, 155

121. Sonber, J. K.; Murthy, T. S. R. Ch.; Subramanian, C.; Fotedar, R. K.; Hubli, R. C.; Suri, A. K. *Trans. Ind. Ceram. Soc.*, **2013,** *72 (2)*, 100-107

122. Markovic, B. T.; Draganic, I.; Vasiljevic´-Radovic, D.; Romc ˇevic, N.; Romcˇevic, M.; Dramic´anin, M.; Markovic, Z. *App. Sur Sc.*, **2007**, *253*, 4029–4035

123. Fathi, A.; EhSani, N.; Rashidzadeh, M.; Baharvandi, H.; Rahimnejad, A. *Silikáty*, **2012**, *56*, 32-35

ISSN: 0971-1260
Vol-22-Issue-16-August-2019

124. Uslu, I.; Tunc, T. *J. Inorg. Organomet. Polym.*, **2012**, *22*, 183–189

125. Ozcelik, B. *J. of Mater. Res.*, **2016**, *31*, 2789-2803