



HAL
open science

Synthesis of boron carbide from its elements at high pressures and high temperatures

A. Chakraborti, N. Vast, Y. Le Godec

► **To cite this version:**

A. Chakraborti, N. Vast, Y. Le Godec. Synthesis of boron carbide from its elements at high pressures and high temperatures. *Solid State Sciences*, 2020, 104, pp.106265. 10.1016/j.solidstatesciences.2020.106265 . hal-03088244

HAL Id: hal-03088244

<https://hal.science/hal-03088244>

Submitted on 21 Jan 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Synthesis of boron carbide from its elements at high pressures and high temperatures

A. Chakraborti^{1,2*}, N. Vast¹, Y. Le Godec²

¹ Laboratoire des Solides Irradiés, École Polytechnique, CEA/DRF/IRAMIS, CNRS UMR 7642, Institut Polytechnique de Paris, 28 route de Saclay, F-91128 Palaiseau cédex, France

² Institut de Minéralogie, Physique des Matériaux et Cosmochimie, Sorbonne Université, 4 Place Jussieu, F-75252 Paris, France

(*amrita.chakraborti@polytechnique.edu)

Abstract

The formation of boron carbide under high pressures and from elemental reactants has been studied. Commercial crystalline β rhombohedral boron and amorphous glassy carbon have been submitted to temperatures ranging from 1 200 °C to 2 200 °C at pressures of 2 GPa and 5 GPa. The experiments have been repeated for crystalline boron and graphite. It turns out that the higher the pressure, the higher the formation temperature of boron carbide. The reaction temperature is also affected by the choice of the reactants. Evidence of intermediate phases has also been found in some of the syntheses.

Keywords

High-pressure high temperature synthesis, boron carbide, the Paris-Edinburgh cell

Introduction

Boron carbide is a widely used hard material that has dual applications ranging from numerous industrial purposes to defence applications like safety armours and bullet-proof jackets.¹ Most of these applications are due to the specificity of the physical properties of this important ceramic material, that combines high hardness (Vickers hardness² of 38 GPa²), low specific density³ (2.52 g/cc) and high chemical stability.^{4,5,1} Moreover, the ¹⁰B nucleus is a powerful neutron absorber, so that elemental boron is used as a neutron moderator in actual nuclear power plants, and boron carbide is expected to be the potential neutron moderator in the possible future French generation IV reactors.

Industrially, boron carbide is formed through carbothermic or magnesiothermic reaction,^{6,3,7} since these processes are among the most economically viable, but the final product is doomed to contain impurities. Contrastingly, producing boron carbide from ultrapure elements -boron and carbon-

results in products of the highest purity.⁶ Thus, elemental synthesis of boron carbide becomes a very important process when the purity of the final product is of paramount importance.

Numerous studies have been performed on the synthesis of boron carbide with various reactants at ambient or low pressures.^{5,6} On the other hand, there have been several studies on the properties of boron carbide crystals at high pressures.^{8,9,10,11,12,13} One study reports the synthesis of ordered boron carbide at 8 GPa but the synthesis reactants are not detailed.¹⁴ However, no study has recorded the synthesis parameters of boron carbide from its elemental components at high pressure as of yet. The purpose of the present study is to fill this gap in the literature.

In fact, high pressure has become a very versatile tool. The introduction of pressure as a synthesis parameter brings up an additional element in the thermodynamic phase space and allows the researchers to access to solid state compounds that could not otherwise be synthesized with traditional low pressure thermodynamic methods.¹⁵ This has led to the discovery of many new phases for different compounds in recent years.^{16,17} Such new phases at high pressure can also be expected from boron carbide. Indeed, *ab initio* studies have already predicted the existence of several new phases of boron carbide under high pressure.^{18,19,20,21}

Thus, a systematic study of the formation of boron carbide at high pressure becomes important in order to fix the optimum parameters for the synthesis, which can further lead to the discovery of new crystalline phases. Moreover, it is also useful to focus on elemental synthesis at the beginning as this, besides leading to the purest products, also simplifies the characterisation process²².

In the present study, we set out to document the optimum parameters of the synthesis of boron carbide from elements (boron and carbon) under mid-range pressures of 2 GPa and 5 GPa. The purpose of this study is to explore the formation of boron carbide from elements at high pressures and fix the parameters of synthesis.

Experimental material and methods

The first set of experiments has been done by mixing crystalline boron (Prolabo, 99.9% purity) and glassy amorphous carbon (Sigma-Aldrich, 99.95% trace metals basis) in the ratio of 4:1. Syntheses have then been done using the large volume Paris-Edinburgh press^{23,24} at two different pressures, 2 GPa and 5 GPa, under temperatures ranging from 1 200°C to 2 400°C for 2 hours each. In Figure 1, we show the schema of the gasket assembly. The fired pyrophyllite gasket is placed between the anvils of the press during compression. Inside the cylindrical hole of the gasket, the furnace made of graphite forms the first layer. The graphite is heated through resistive heating, thus leading to the high values of the temperature generated in the experiments. Next, hexagonal boron nitride hollow cylinders and caps are used to electrically isolate the sample from the graphite furnace. Numerous experiments have shown that hexagonal boron nitride does not react with boron nor carbon in the (P,T) range investigated in our study.^{25,26} In the vertical cross-sections, the graphite caps, which are used as part

of the furnace, are then covered with molybdenum discs to ensure the conductivity of the electrical current. Finally, the top layer is formed with ceramic inside inox rings, which ensures again that the electric current required for resistive heating is unhindered. The system inside the gasket is designed to be symmetric.

After the synthesis, the products have been quenched and the sample has been decompressed. The benefit of using a large volume press is that enough volume is produced, so that one can extract the product from the gasket and apply *ex-situ* characterisation techniques on it. Therefore, after each such experiment, the gasket has been broken carefully and the product synthesized has been recovered. Then, they have been characterised *ex-situ* through x-ray diffraction in a Rigaku diffractometer. Raman spectroscopy (not shown) has been used as a secondary characterisation technique to validate the results obtained by x-ray diffraction. The process of the sample recovery from the gasket led sometimes to the presence of some amount of boron nitride in the product, since boron nitride tubes formed the innermost part of the gasket assembly that held the reactants²⁷.

The same set of experiments has then been repeated after changing the reactant mix - crystalline boron and graphite (Goodfellow, 99.997% purity). All the other parameters of the experiments have been kept identical.

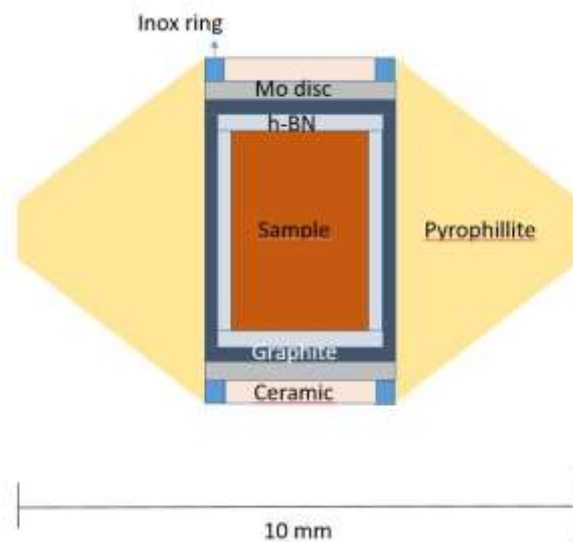


Figure 1: schema of the set-up assembly used in the Paris Edinburg cell for the syntheses. It shows the fired pyrophyllite pressure transmitting medium, the graphite furnace, the chemically inert hexagonal boron nitride capsule with the sample inside. The furnace is covered by molybdenum rings and inox rings filled with ceramic to ensure electrical conductivity for resistive heating.

Results

From the scientific literature, it has been observed that boron carbide forms from commercial β boron and graphite at temperatures around 1 300 °C under pressure values smaller than 50 MPa.^{28,29} However, so far, there has been no study using different allotropes of elemental boron or carbon. The allotropes do affect the initiation temperature, as our study is going to show.

The duration of the synthesis has been kept to be 2 hours, since that was the maximum duration of synthesis found in the literature.³⁰ This is expected to allow enough time for the elemental boron and carbon to diffuse and produce solid state reaction to form boron carbide.

The x-ray diffraction (XRD) of the synthesis from crystalline boron and amorphous carbon at 2 GPa, as reported in Figure 2, shows only the presence of β boron at 1 200°C and 1 400°C. No boron carbide has been formed at these temperatures. At 1 800°C, significant change occurs in the XRD, as boron carbide forms. This tendency continues up to the final synthesis temperature of 2 200 °C, as the intensity of the boron carbide peaks becomes stronger, while the intensity of the β boron peaks diminishes.

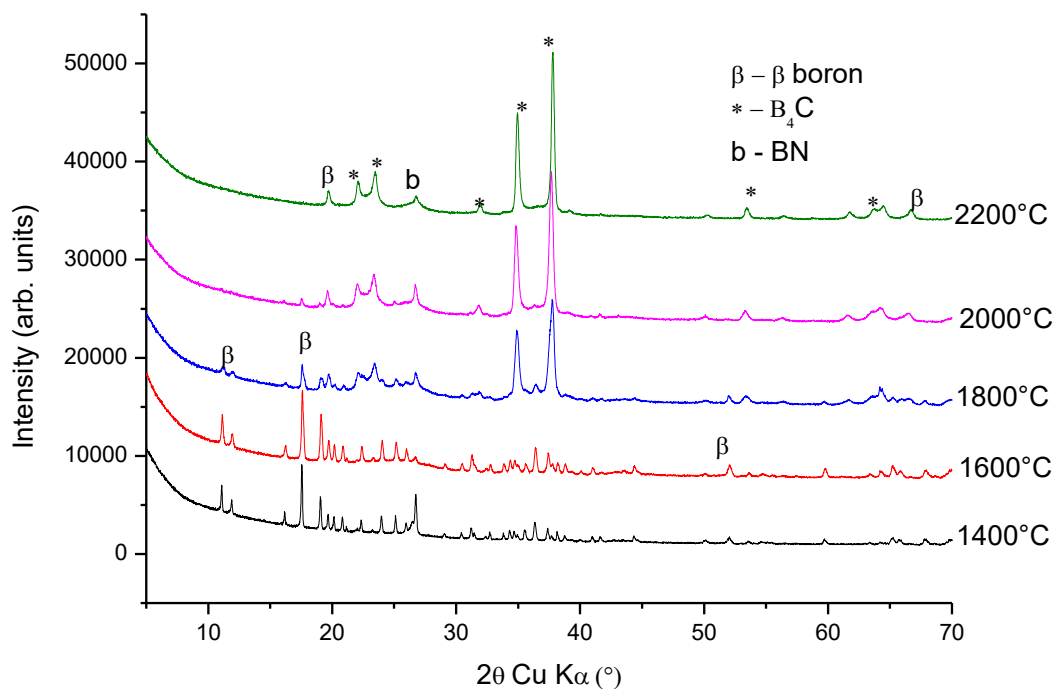


Figure 2: *ex-situ* x-ray diffraction pattern of quenched sample from a mixture of crystalline boron and amorphous carbon under 2 GPa in the Paris-Edinburgh cell for 2 hours at various temperatures.

At 5 GPa, the temperature of the product formation varies significantly from what has been reported above for 2 GPa. Strong intermediate phases are present at 1 800 °C. Unlike what has been seen in the above-mentioned 2 GPa synthesis, boron carbide is not formed at 1 800 °C. Instead, the temperature of formation of boron shifts to higher temperature, 2 000 °C for the 5 GPa synthesis. Finally, at 2 200 °C, boron carbide becomes the most prominent phase. The diffraction pattern at

2 200 °C for both the 2 GPa and 5 GPa syntheses appear to be similar, but evidently, they went through different mechanisms to reach the same ultimate product of boron carbide. In Figure 3, we show the XRD pattern at different temperatures for the 5 GPa series.

In the next step, the syntheses have been repeated with graphite (instead of amorphous carbon) and the same crystalline β boron. In this case, at 2 GPa, the synthesis temperature of boron carbide rises to 2 000 °C. In Figure 4, we report the XRD pattern comparing the synthesis of boron carbide from amorphous carbon (at 1 800 °C) and from graphite (at 2 000 °C).

For the syntheses at 5 GPa, the temperature of formation of boron carbide with graphite increases as well. In addition, we find no strong prominence of intermediate phases before boron carbide is formed. In Figure 5, we report the comparison between the synthesis from crystalline boron and amorphous carbon and the synthesis from crystalline boron and graphite.

In Table 1, we summarise the synthesis temperatures of boron carbide from various elemental reactants and pressures.

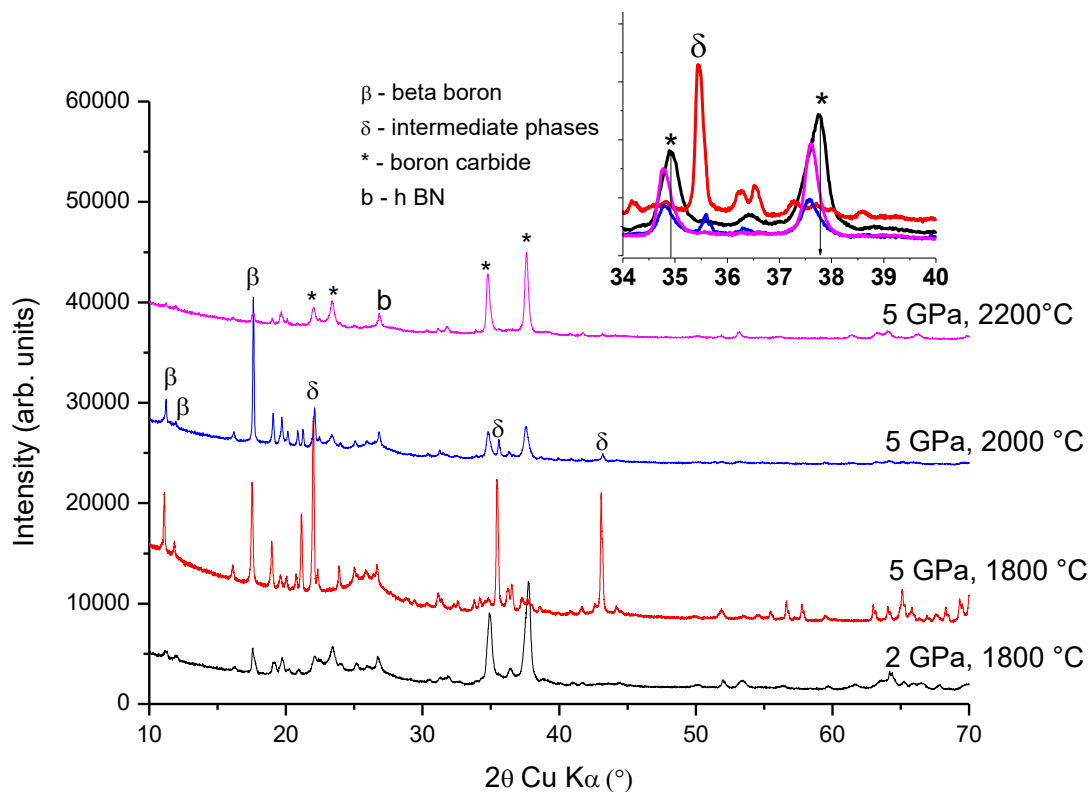


Figure 3: ex-situ x-ray diffraction pattern of quenched sample from a mixture of crystalline boron and amorphous carbon under 5 GPa for 2 hours. Since β boron has numerous peaks, only the most prominent ones have been marked – all the unmarked peaks are those of β boron. The inset is the zoom between 34 $^\circ$ and 40 $^\circ$, of the superposition of the curves of the main figure, to facilitate the comparison

of the synthesis of boron carbide at 1 800 °C for 2 GPa, and the 5 GPa synthesis at 1 800 °. The latter shows intermediate phases, but no boron carbide is present.

Pressure	Reactants	Temperature of formation of B ₄ C
2 GPa	Crystalline boron + Amorphous carbon	1 800 °C
2 GPa	Crystalline boron + Graphite	2 000 °C
5 GPa	Crystalline boron + Amorphous carbon	2 000 °C
5 GPa	Crystalline boron + Graphite	2 200 °C

Table 1: summary of the synthesis temperatures of boron carbide from elemental boron and carbon, depending on the pressure and on the solid-state form of carbon.

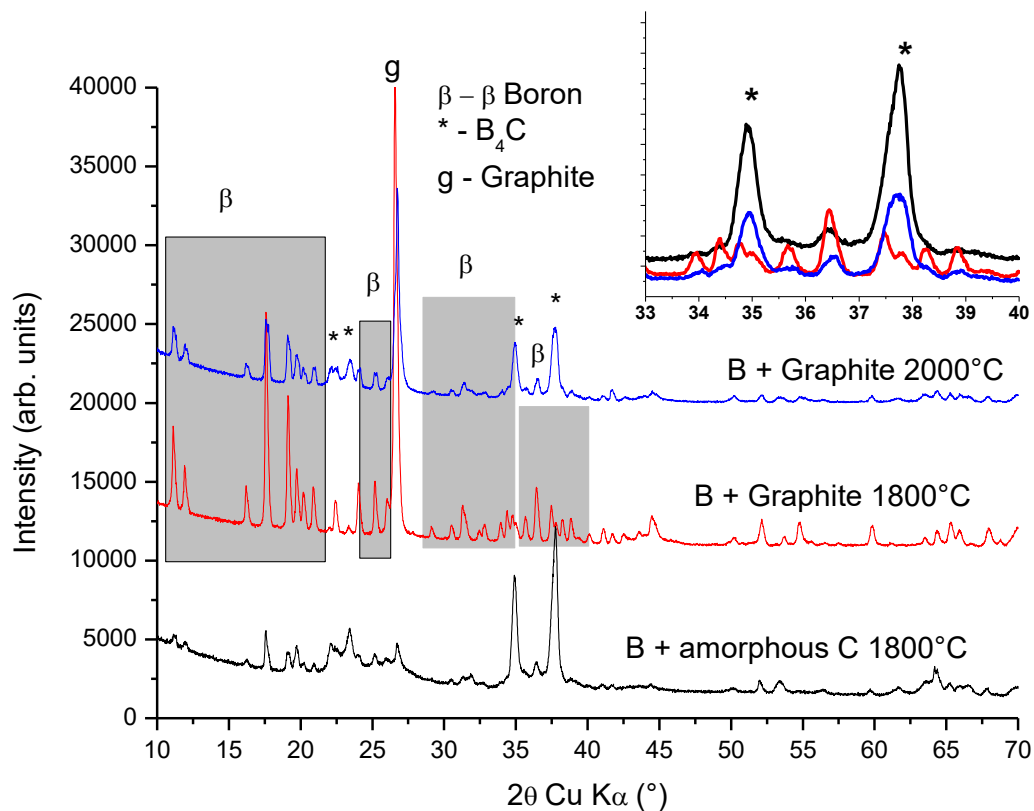


Figure 4: ex-situ x-ray diffraction pattern of quenched samples from a mixture of crystalline boron and graphite under 2 GPa for 2 hours. The inset is the zoom between 33 ° and 40 ° of the superposition of

the curves of the main figure (same colours). It shows the formation of boron carbide at 1 800 °C for the amorphous carbon reactant, but no boron carbide is present with graphite at 1 800 °C.

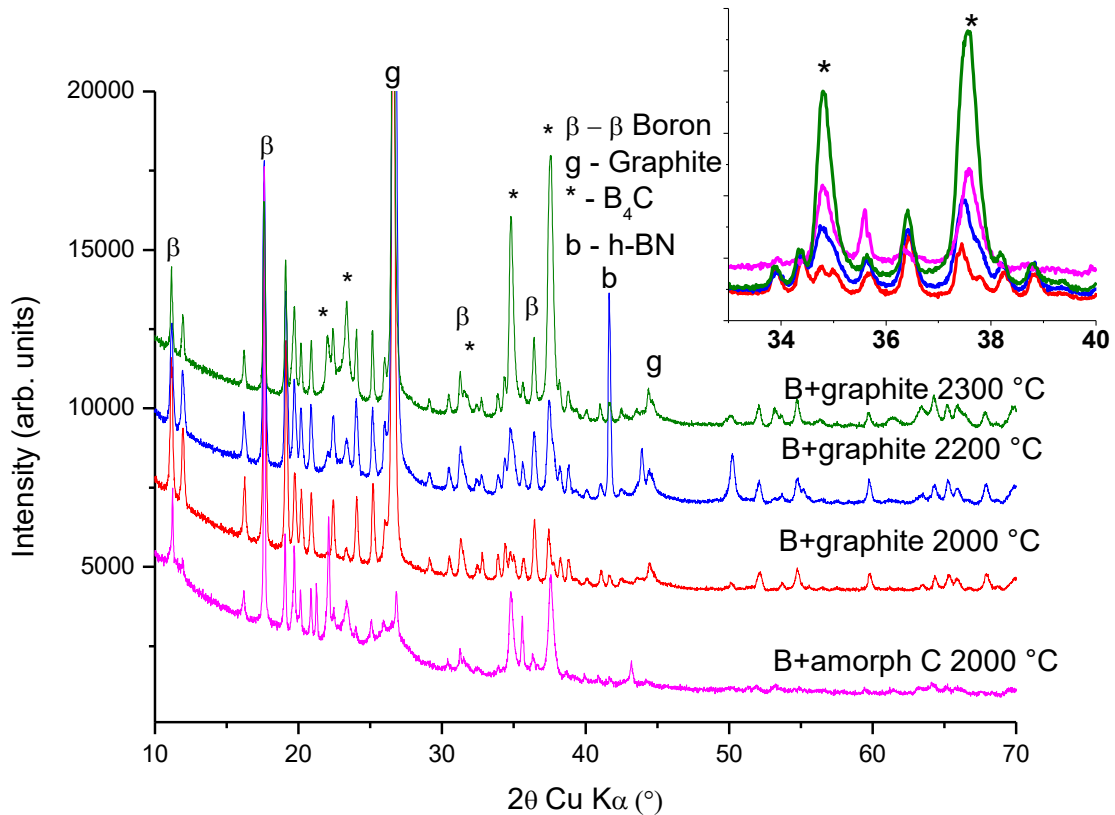


Figure 5: ex-situ x-ray diffraction pattern of quenched sample from the mixture of crystalline boron and graphite under 5 GPa for 2 hours. The inset is the zoom between 33 ° and 40 ° of the superposition of the curves of the main figure (same colours). It is shown that boron carbide is formed at 2 000 °C with the amorphous carbon reactant, and only at 2 200 °C with the graphite reactant.

Discussions

The synthesis at 2 GPa follows a straightforward trajectory, similar to what has been reported in the literature^{29,30} for the low pressure syntheses. However, the synthesis temperature rises considerably. The 1 200 °C and 1 400 °C results have β boron only, and no boron carbide. A temperature increase by more than 400 ° w.r.t. ambient pressure is required to form boron carbide at 2 GPa. Only by 1 800 °C (in the case of amorphous carbon) and 2 000 °C (in the case of graphite) do we find that boron carbide has formed.

For the 5 GPa syntheses with amorphous carbon, there is an increase in the intensity of a single β boron peak at 2 000 °C before it vanishes at 2 200 °C. This may be caused by the increase in the grain size at high temperatures due to the sintering of β boron.^{31,32} The products at 1 200 °C and 1 400 °C were powdery, while those at 1 800 °C, 2 000 °C and 2 200 °C were sintered and granular, which might have led to the prominence of certain peaks in the diffraction pattern.

We have found that amorphous carbon is a better reactant than graphite for synthesizing boron carbide at elevated pressures, since the use of graphite requires a further increase of the synthesis temperature.

The synthesis temperature also increases with the increase of pressure in all of the cases. A possible explanation for this might be that the high pressure inhibits the diffusion of boron and carbon atoms and thus slows down the reaction. This requires the presence of higher temperatures to help the diffusion process before the formation of boron carbide can take place.

However, this explanation raises an interesting question for the syntheses at eventually higher values of the pressure. If the temperature of formation continues to increase, it can eventually intersect the melting curve of boron carbide at high pressures.¹⁰ In that case, the temperature needed to offset the hindrance to the diffusion of boron and carbon atoms at high pressure may lie above the melting point of boron carbide in the respective pressure region – this may lead to new mechanisms of boron carbide formation under these pressure conditions.

Conclusions

The optimum synthesis parameters of boron carbide at high pressures (up to 5 GPa) from elemental boron and carbon has been studied for the first time, using the large volume Paris-Edinburgh press.

This study has shown that the mechanism of elemental formation of boron carbide is heavily dependent on pressure, which affects the temperature of formation of boron carbide. In the near future, we will study the other end of the industrially available high-pressure region, 10 GPa – 20 GPa, using multi-anvil cells, in order to observe the effect of high pressure on the formation temperature of boron carbide.

Amorphous carbon has proven to be a better reactant than graphite for the synthesis of boron carbide, since it lowers the temperature of formation, both at 2 GPa and at 5 GPa. We will next explore the synthesis parameters with amorphous boron instead of crystalline β boron, in order to study how the use of amorphous boron affects the formation temperature of boron carbide.

Acknowledgement

Supports from the DGA (France) and from the program NEEDS-Matériaux (France) are gratefully acknowledged. Useful discussions with Benoit Baptiste, Antoine Jay, and Silvia Pandolfi are acknowledged.

References

1. Caretti, I., Gago, R., Albella, J. M. & Jiménez, I. Boron carbides formed by coevaporation of B and C atoms: Vapor reactivity, B_xC_{1-x} composition, and bonding structure. *Phys. Rev. B* **77**, 174109 (2008).
2. Herrmann, M., Sigalas, I., Thiele, M., Mueller, M., Kleebe, H.-J., Michaelis, A. Boron suboxide ultrahard materials. *International Journal of Refractory Metals and Hard Materials* **39**, 53–60 (2013).
3. Roy, T. K., Subramanian, C. & Suri, A. K. Pressureless sintering of boron carbide. *Ceram. Int.* **32**, 227–233 (2006).
4. Kakiage, M., Tominaga, Y., Yanase, I. & Kobayashi, H. Synthesis of boron carbide powder in relation to composition and structural homogeneity of precursor using condensed boric acid–polyol product. *Powder Technol.* **221**, 257–263 (2012).
5. Thévenot, F. *Boron Carbide - A Comprehensive Review. Journal of the European Ceramic Society* v6, 205-225 (1990).
6. Suri, A. K., Subramanian, C., K Sonber, J. & Murthy, T. S. R. C. *Synthesis and Consolidation of Boron Carbide: A Review. International Materials Reviews* **55**, 4-40 (2010).
7. Alizadeh, A., Taheri-Nassaj, E., Ehsani, N. & Baharvandi, H. R. Production of boron carbide powder by carbothermic reduction from boron oxide and petroleum coke or carbon active. *Adv. Appl. Ceram.* **105**, 291–296 (2006).
8. Yan, X. Q., Tang, Z., Zhang, L., Guo, J. J., Jin, C. Q., Zhang, Y., Goto, T., McCauley, J. W., Chen, M. W. Depressurization amorphization of single-crystal boron carbide. *Phys. Rev. Lett.* **102**, 075505 (2009).
9. Fujii, T., Mori, Y., Hyodo, H. & Kimura, K. X-ray diffraction study of B_4C under high pressure. *Journal of Physics: Conference Series* **215**, 012011 (2010).
10. Mukhanov, V.A., Sokolov, P.S. & Solozhenko, V.L. On melting of B_4C boron carbide under pressure. *J. Superhard Mater.* **34**, 211–213 (2012)
11. Dera, P., Manghnani, M. H., Hushur, A., Hu, Y. & Tkachev, S. New insights into the enigma of boron carbide inverse molecular behavior. *J. Solid State Chem.* **215**, 85–93 (2014).
12. Hushur, A., Manghnani, M. H., Werheit, H., Dera, P. & Williams, Q. High-pressure phase transition makes $B_{4.3}C$ boron carbide a wide-gap semiconductor. *J. Phys. Condens. Matter* **28**, 4 (2016).
13. Werheit, H., Manghnani, M. H., Kuhlmann, U., Hushur, A. & Shalamberidze, S. Mode Grüneisen parameters of boron carbide. *Solid State Sci.* **72**, 80–93 (2017).

14. Mondal, S., Bykova, E., Dey, S., Ali S. I., Dubrovinskaia, N., Dubrovinsky, L., Parakhonskiy, G., van Smaalen, S. Disorder and defects are not intrinsic to boron carbide. *Sci. Rep.* **6**, 19330 (2016).
15. Schilling, J. S. The use of high pressure in basic and materials science. *J. Phys. Chem. Solids* **59**, 553–568 (1998).
16. Solozhenko, V. L., Kurakevych, O., Andrault, D., Le Godec, Y. & Mezouar, M. Ultimate metastable solubility of boron in diamond: Synthesis of superhard diamondlike BC₅. *Phys. Rev. Lett.* **102**, 015506 (2009).
17. Pandolfi, S., Renero-Lecuna, C., Le Godec, Y., Baptiste, B., Menguy, N., Lazzeri, M., Gervais, C., Spektor, K., Crichton W.A., Kurakevych, O. Nature of Hexagonal Silicon Forming via High-Pressure Synthesis: Nanostructured Hexagonal 4H Polytype. *Nano Lett.* **18**, 5989–5995 (2018).
18. Vast, N., Sjakste, J. & Betranhandy, E. Boron carbides from first principles. *J. Phys. Conf. Ser.* **176**, 012002 (2009).
19. Jay, A., Vast, N., Sjakste, J. & Duparc, O. H. Carbon-rich icosahedral boron carbide designed from first principles. *Appl. Phys. Lett.* **105**, 031914 (2014).
20. Jay, A. *In silico design of a new phase of boron carbide*, Ph.D. thesis, École Polytechnique, Palaiseau (2014).
21. Ektarawong, A., Simak, S. I. & Alling, B. Carbon-rich icosahedral boron carbides beyond B₄C and their thermodynamic stabilities at high temperature and pressure from first principles. *Phys. Rev. B* **94**, 054104 (2016).
22. Anselmi-Tamburini, U., Munir, Z.A., Kodera, Y., Imai, T. and Ohyanagi, M. (2005), Influence of Synthesis Temperature on the Defect Structure of Boron Carbide: Experimental and Modeling Studies. *Journal of the American Ceramic Society*, **88**: 1382-1387.
23. Klotz, S., Hamel, G. & Frelat, J. A new type of compact large-capacity press for neutron and x-ray scattering. *High Press. Res.* **24**, 219–223 (2004).
24. Lacomba-Perales, R., Martínez-García, D., Errandonea, D., Le Godec, Y., Philippe, J., Le Marchand, G., Chervin, J.C., Polian, A., Muñoz, A., López-Solano, J. Experimental and theoretical investigation of the stability of the monoclinic BaWO₄-II phase at high pressure and high temperature. *Phys. Rev. B* **81**, 144117 (2010).
25. Hubert, H., Garvie, L., Devouard, B., Buseck, P. R., Petuskey, W., McMillan, P. F. High-Pressure, High-Temperature Synthesis and Characterization of Boron Suboxide (B₆O). *Chem. Mater.* **10**, 1530-1537 (1998).
26. Zhao, J., Yang, L., Li, F., Yu, R. & Jin, C. Structural evolution in the graphitization process of activated carbon by high-pressure sintering. *Carbon* **47**, 744–751 (2009).
27. Mezouar, M., Bihan, T., Libotte, H., Le Godec, Y., Häusermann, D. Paris–Edinburgh large-volume cell coupled with a fast imaging-plate system for structural investigation at high pressure and high temperature. *J. Synchrotron Radiat.* **6**, 1115–1119 (1999).
28. Roszeitis, S., Feng, B., Martin, H.-P. & Michaelis, A. Reactive sintering process and thermoelectric properties of boron rich boron carbides. *J. Eur. Ceram. Soc.* **34**, 327–336

(2014).

29. B. Wang, C., Zhang, S., Shen, Q. & M. Zhang, L. *Investigation on reactive sintering process of boron carbide ceramics by XRD. Materials Science and Technology* **25**, 809-812 (2009).
30. Werheit, H. & Shalamberidze, S. Advanced microstructure of boron carbide. *J. Phys. Condens. Matter* **24**, 385406 (2012).
31. Guo, L., Huang, M. & Zhang, X. Effects of sintering temperature on structure of hydroxyapatite studied with Rietveld method. *J. Mater. Sci. Mater. Med.* **14**, 817–822 (2003).
32. Zhang, J., Huang, X., Zhang, H., Xue, Q., Xu., Wang, L., Feng, Zongyu. The effect of powder grain size on the microstructure and electrical properties of 8 mol% Y₂O₃-stabilized ZrO₂. *RSC Adv.* **7**, 39153–39159 (2017).