

# Optimization of the Synthesis of Boron Suboxide Powders

Enoch N. Ogunmuyiwa\*, Oluwagbenga T. Johnson, *Member, IAENG*, Iakovos Sigalas, Mathias Hermann and Ayo S. Afolabi, *Member, IAENG*

**Abstract**— B<sub>6</sub>O powders were produced from the reaction between boric acid and amorphous boron powders at the reaction temperatures between 300 and 1400°C for 6 hours. The powders produced were characterized in terms of particle size, phase analysis and composition, product yield as well as morphology. Increase in temperature increases both the yield as well as the particle size of the produced powders. XRD pattern obtained also showed improved crystallinity of the produced powder as the temperature increases. SEM image obtained at higher temperature clearly showed improved crystallinity (star-like crystals) as the reaction temperature was increased. The B<sub>6</sub>O powders synthesised at 1300°C for 6 hours had the optimum yield of over 95%.

**Keywords** — Boron suboxide, Synthesis, Morphology, Crystallinity.

## I. INTRODUCTION

DIAMOND and cubic boron nitride (cBN) are the superhard materials currently used in industrial applications. However, these materials utilize ultra-high temperature and pressure to manufacture, thus making their production expensive. Although these materials combine excellent chemical, mechanical, and physical properties, their applications are limited at high temperatures. Diamond cannot be used as a cutting tool for ferrous alloys at high temperatures while an increase in temperature weakens cBN and transforms it to its hexagonal structure (hBN) [1]. These problems with the current superhard materials have stimulated research into finding new superhard materials (with properties comparable to or even superior to those of diamond and cBN) for industrial applications.

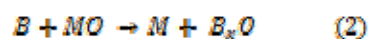
Boron suboxide (nominally B<sub>6</sub>O) has been found to possess properties that indicates its potential use as an industrial superhard material. A single crystal of B<sub>6</sub>O has a hardness of 45 GPa and a fracture toughness of 4.5 MPa.m<sup>0.5</sup> [2], approaching that of single crystal diamond at

5 MPa.m<sup>0.5</sup> and significantly better than that of a single crystal of cBN at 2.8 MPa.m<sup>0.5</sup> [3]. B<sub>6</sub>O has a better thermal stability compared to that of diamond [2, 4] and can be produced without high pressure [5–8]. All these properties suggest that B<sub>6</sub>O may be a good candidate for cutting tool and other wear part applications where abrasive wear resistance is important.

Several publications and patents have reported that B<sub>6</sub>O powder can be produced mainly via two techniques: the reaction of boron with boron oxide (B<sub>2</sub>O<sub>3</sub>) at moderately high temperatures and pressure, and the reaction of boron with a metal oxide at temperatures ranging between 1200°C to 1500°C at ambient pressure. Ellison-Hayashi et al., [9] reported that B<sub>6</sub>O powder can be produced by reacting elemental boron with boron oxide between 1900 and 2100°C, under a pressure of between 21 and 28 MPa, while Oloffson and Lundstrom [10], suggested a temperature between 1000 and 2000°C with the reaction in equation 1.



The second technique (by reacting boron with metal oxide) can be performed at between a temperatures of 1200 and 2000°C via a low pressure [11–12], and at a high pressure of about 3.5 GPa [13]. The reaction of boron powder with metal oxide is represented in equation 2.



Where M could be metals from zinc (Zn), magnesium (Mg), cadmium (Cd), Gallium (Ga), chromium (Cr), copper (Cu), bismuth (Bi), and indium (In) [10, 14]. In the production of B<sub>6</sub>O powders through this reaction, zinc oxide (ZnO) has gained acceptance due to the ease with which the undesired products and reactants can be removed. The Zn is removed from the crucible in gaseous form while the ZnO and excess boron powder can be removed by washing in hydrochloric acid. Also, at the reaction temperature, ZnO is a liquid phase and so would increase the rates of reaction via increased mass transport rates [12].

The replacement of diamond and cBN by B<sub>6</sub>O in industrial applications primarily depends on the commercialization of an economically viable method of its manufacture. Such a method has already been developed and involves the reduction of boric acid with amorphous boron under ambient pressure. The method has however never been thoroughly investigated and optimized as much research concerning B<sub>6</sub>O has dwelled on improving its hardness and toughness properties. This research is therefore focused on the optimization of this technology that would therefore translate to a much more affordable method of bulk production of B<sub>6</sub>O powders for industrial use.

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EN Ogunmuyiwa\* and AS Afolabi are both with the Department of Civil and Chemical Engineering, University of South Africa, Florida Campus, Johannesburg, South Africa. (\*Corresponding author: phone: +27-79-838-1218; e-mail: ogunmen@unisa.ac.za, afoalaas@unisa.ac.za).

OT Johnson is with the Department of Mining and Metallurgical Engineering, University of Namibia, Ongwediva Campus, Namibia. (e-mail: ojohnson@unam.na, Johnson.gbenga@gmail.com).

I Sigalas is with the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa. (e-mail: iakovos.sigalas@wits.ac.za).

M. Herrmann is with the Fraunhofer Institute of Ceramic Technologies and Systems, Winterbergstrasse 28, D-01277, Dresden, Germany. (e-mail: Mathias.Herrmann@ikts.fraunhofer.de).

## II. METHODOLOGY

The B<sub>6</sub>O powder used in this study was produced from the reaction of boric acid (H<sub>3</sub>BO<sub>3</sub>; 99% purity, from Sigma-Aldrich and amorphous boron powder (B; 95–97% purity, from Sigma-Aldrich) as described elsewhere [10, 15–16]. Prior to the synthesis, a stoichiometric amount of H<sub>3</sub>BO<sub>3</sub> and B were weighed out using a mass balance. An excess amount of 3% of H<sub>3</sub>BO<sub>3</sub> was added in order to compensate for the evaporation of B<sub>2</sub>O<sub>3</sub> during the reaction.

About 50 g of the reagents were mixed in a tubular mixer for approximately 2 hours to ensure a homogenous mixture, this is necessary as it ensures similar reaction kinetics throughout the mixture. 20 g of the mixture was weighed out into the alumina boat, filled such that it is leveled at the center and loosely filled at the sides. The alumina boat was firstly washed with propanol prior to the first run and with distilled water thereafter and then air dried. The alumina boat was coated on the outside with hexagonal boron nitride (hBN) in order to prevent it sintering onto the inside of the tube furnace upon the condensation of the residual boric acid vapor during cooling. The boat had to be placed upside down during coating in order to ensure that the boron nitride particles do not enter into the boat and consequently contaminate the sample.

The mixture was then heated in a tube furnace under argon at temperatures between 300 and 1400°C for 6 hours at ambient pressure. The products were then transferred into a beaker and distilled water added to ensure washing of residual B<sub>2</sub>O<sub>3</sub> and other soluble contaminants. The washed product was then heated at a temperature of about 60°C, while stirring at a speed of 400 rpm using a magnetic stirrer. The product was washed twice (under each condition) for about 2 hours and left to settle for about 16 hours and thereafter decanted. The decanted product (B<sub>6</sub>O powder) was then dried and weighed on a mass meter in order to determine the yield. A small sample of the product was also used for XRD, particle size analysis and the SEM analysis.

The particle size of the milled powder was measured using a Mastersizer 2000 (Malvern Instruments, Germany), with the d<sub>10</sub> and d<sub>50</sub> sizes of the powders recorded. X-ray diffraction (XRD) was performed on a Philips PW 1713 fitted with a monochromatic Cu K $\alpha$  radiation set at 40 kV and 20 mA in the 2 $\theta$  range of 10 – 90 degrees, and the phase identification with X'Pert HighScore. The microstructural changes was investigated in an environmental scanning electron microscope (Philips ESEM XL30) equipped with energy dispersive X-ray spectrometer (EDX) for various elemental compositions found in the materials.

## III. RESULTS

Table 1 shows the summary of the resulting properties of the produced B<sub>6</sub>O powders at the reaction temperatures between 300 and 1400°C. The trend shows that as the reaction temperatures is increased, so does the particle size and the yield. The increase in particle size was particularly significant above the reaction temperature of 1100°C whereby it is observed that the d<sub>50</sub> jumped from a value just below 3  $\mu$ m to above 10  $\mu$ m.

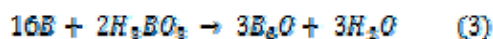
The yield of the B<sub>6</sub>O powder obtained at the various reaction conditions was primarily influenced by the method of washing and the purity of the powder. The washing

resulted in loses of some of the B<sub>6</sub>O powder, specifically the lighter particles that did not settle fast enough within the time that each batch powder was allowed to stand after washing. This effect was mainly observed for the B<sub>6</sub>O that was produced at the reaction temperature of 1100°C and below (Figure 3). Such loses were also experienced with the B<sub>6</sub>O powder produced at higher temperatures, though it was not as extensive. Another factor which could influence the calculated yield was the actual purity of the powder produced. It is shown by the XRD analysis (Figure 1) that some of the B<sub>6</sub>O powders produced also contained other constituents than B<sub>6</sub>O. In such cases the calculated yield was then not a true reflection of the actual B<sub>6</sub>O that was produced at the particular reaction

Table 1 Properties of produced B<sub>6</sub>O powders

Temperature (°C)	d <sub>10</sub> ( $\mu$ m)	d <sub>50</sub> ( $\mu$ m)	Yield (%)
300	1.02	2.73	43.10
400	1.20	2.84	47.63
750	0.98	2.67	53.20
1100	0.69	2.00	83.82
1300	1.72	10.53	95.18
1400	1.70	11.01	88.84

Figure 1(a – e) shows the XRD pattern of the produced B<sub>6</sub>O powders at different temperature between 300 and 1400°C at the reaction time of 6 hours. From the pattern, it was observed that the amorphous nature of the produced B<sub>6</sub>O powders decreases with increasing temperatures. At temperatures below 750°C, only boron major peaks were obtained. The decomposition of H<sub>3</sub>BO<sub>3</sub> to form H<sub>2</sub>O and B<sub>2</sub>O<sub>3</sub> had already begun at approximately 160°C [17] making B<sub>2</sub>O<sub>3</sub> available for the reaction with B according to equation 3.



However, from Figure 1(a) only the crystallisation of B occurred and very little, if any, B<sub>6</sub>O was formed at this reaction temperature below 750°C. The B peaks further show that crystallisation of amorphous B that occurred resulted in the formation of tetrahedral and rhombohedral B phases. The absence of B<sub>6</sub>O is most likely owed to the fact that the energy available at this temperature was not sufficient to initiate the crystallisation of B and still overcome the energy barrier for the reaction between B<sub>2</sub>O<sub>3</sub> and B thereafter. B<sub>6</sub>O was however detected by the XRD at the reaction temperatures of 750°C and above Figure 1(b – e), though small peaks of B were still present. Comparison of the Figure 1 (a–e), shows that the crystallinity of the powder increased as temperature increases.

## IV. DISCUSSION

This study investigated the effect of varying temperature on the production of B<sub>6</sub>O powder. Figure 2 shows the influence of temperature on the particle size and the percentage yield. The observed result are much anticipated since an increase in temperature results in an increased kinetic energy of the system on a micro scale, and thus an increased tendency for diffusion to occur thus making the atoms travel longer distances during diffusion. Increased

diffusion favours crystal growth to form clusters as an initiative to minimise the overall energy of the system. Higher reaction temperatures therefore primarily results in larger  $B_2O_3$  sub-crystals, recalling the fact that this particular ceramic is non-stoichiometric when produced under ambient pressure. A higher energy of the system helps break the energy barriers hindering grain growth, especially the energy required for grain boundary diffusion to occur.

Consequently smaller crystals are consumed by larger ones as grain boundaries expand so that significantly larger crystals are formed. The increasing energy of the system as a result of the reaction temperature also results in significant diffusion on a macro scale so that  $B_2O_3$  particles are able agglomerate forming larger  $B_2O_3$  particles at the given reaction time.

Figure 3 also showed significantly larger particle size were apparent at temperature of  $1300^{\circ}C$  and above. It is envisaged that most of the energy of the system at the reaction temperature  $1100^{\circ}C$  and below was supposedly used to initiate the reaction for the production of  $B_2O_3$  so that very little energy was available to thereafter promote grain growth.

XRD results (Figure 1) showed that the  $B_2O_3$  powders obtained at the temperature  $1100^{\circ}C$  and below contained B, Al-compounds along with  $B_2O_3$ . Furthermore, the XRD obtained at  $300^{\circ}C$  showed only the presence of crystallised B and no  $B_2O_3$  peaks. The yield that was calculated for these products was therefore a poor indication of the actual  $B_2O_3$  produced. Hence, it can be deduced that the yield produced at these conditions was very low based on the quality of the powder obtained. At the reaction temperature of  $1300^{\circ}C$  and above, the quality of the powder obtained during the reaction time was much better (Figure 1). The XRD peaks of these products did not show the presence of any Al-B compounds, which is thought to have been contamination by the alumina boat.

The SEM images of the  $B_2O_3$  powders obtained at the reaction time of 6 hours as shown in figures 3(a – d) clearly outline the fact that crystallinity improved as the reaction temperature was increased. Figure 3(a & b) does not clearly show the presence of star-shaped  $B_2O_3$  crystals due to the presence of amorphous B co-existing with  $B_2O_3$  at these reaction temperatures ( $750$  and  $1100^{\circ}C$ ), as confirmed by the XRD. Figure 3(c & d) shows a better star-shaped, crystal structures of the  $B_2O_3$  powders produced at the reaction temperatures of  $1300$  and  $1400^{\circ}C$  respectively, with much superior crystal obtained at  $1400^{\circ}C$ . It is theoretically reported that the most stable form of  $B_2O_3$  has a crystal rhombohedral structure and it can therefore be assumed that the star-shaped structure is formed as a result of the long-range ordering of a number of single rhombohedral crystals [18–19].

The  $B_2O_3$  crystals formed (Figure 3(a–d)) are not perfect due to the obstacles encountered during their growth, especially the presence of impurities during the reaction. The presence of impurities implies the predominance of a heterogeneous nucleation in the crystallisation of the  $B_2O_3$  powders. The star-like crystals are less defined at the reaction temperature of  $1300^{\circ}C$  and below. This is perhaps the best indication that crystallinity is improved with increasing reaction temperature. A better crystallinity of  $B_2O_3$  is desirable as it implies a more discrete physical properties [18–19], thus making its use more practical for proposed industrial applications. Superior crystallinity is

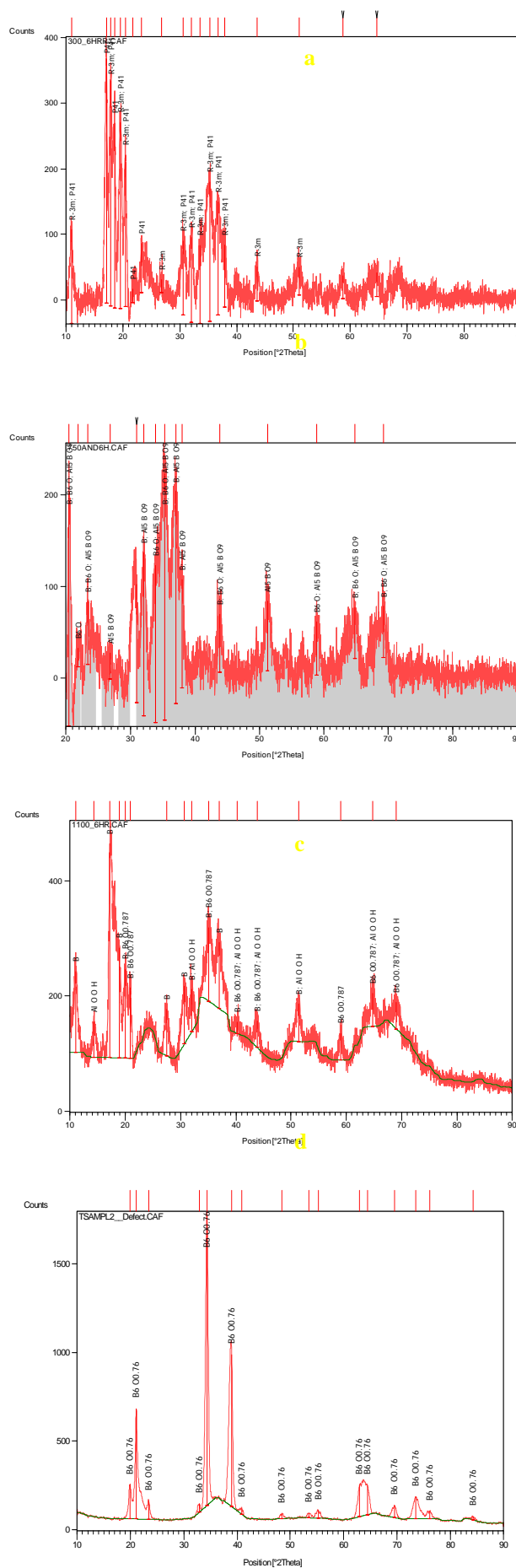


Figure 1 XRD pattern of the  $B_2O_3$  powders obtained at (a)  $300$ , (b)  $750$ , (c)  $1100$ , (d)  $1300$ , and (e)  $1400^{\circ}C$  respectively.

also expected to improve the mechanical properties of the compacts of this B<sub>6</sub>O powder such as the hardness. Thus far high crystallinity has only been achievable by high pressure methods of the production of B<sub>6</sub>O [18], which are rather costly and thus less industrially marketable. This is therefore a very desirable result towards the development of a more marketable method of producing B<sub>6</sub>O.

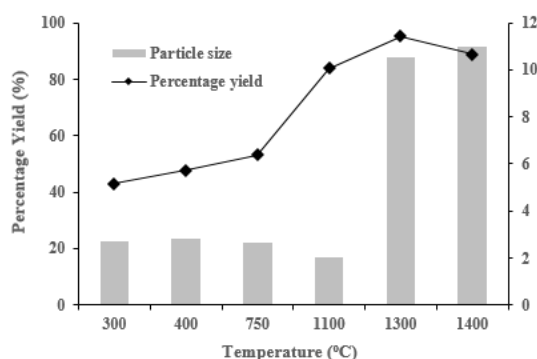


Figure 2 Effect of temperature variations of B<sub>6</sub>O powders on particle size and the percentage yield.

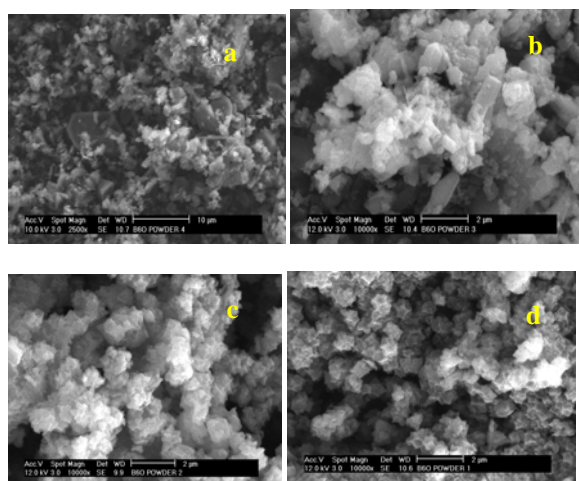


Figure 3 SEM images of B<sub>6</sub>O powders at (a) 750, (b) 1100, (c) 1300, and (d) 1400°C reaction temperatures respectively.

#### V. CONCLUSIONS

B<sub>6</sub>O powders were produced at the reaction temperatures between 300 and 1400°C for 6 hours. XRD analysis showed that the purity of the powders increases with reaction temperature with corresponding increase in the particle size. SEM image obtained at higher temperature clearly showed improved crystallinity (star-like crystals) as the reaction temperature was increased. The B<sub>6</sub>O powders synthesised at 1300°C for 6 hours had the optimum yield of over 95%.

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#### REFERENCES

- [1] A Zerr and R Riedel. Introduction: Novel ultrahard materials, In: Handbook of ceramic hard materials, [ed.] R. Riedel, Wiley-VCH GmbH, Germany. Vol. 1, 45–73.
- [2] D He, Y Zhao, L Daemen, J Qian, and TD Shen. Boron suboxide: As hard as cubic boron nitride. Applied Physics Letters, 81 (2002); (4) 643–645.
- [3] CA Brookes. Mechanical properties of cubic boron nitride – a perspective. Institute of Physics Conference Series, 75 (1986); 207–220.
- [4] D He, M Akaishi, BI Scott and Y Zhao. Growth of boron suboxide crystals in the B-B<sub>2</sub>O<sub>3</sub> system at high pressure and high temperature. Journal of Materials Research 17 (2002); 284–290.
- [5] TC Shabalala, DS McLachlan, I Sigalas, and M Herrmann. Hard and tough boron suboxide based composite. Ceramics International, 34 (2008); 1713–1717.
- [6] A Andrews, M Herrmann, TC Shabalala, and I Sigalas. Liquid phase assisted hot pressing of boron suboxide materials. Journal of European Ceramics Society, 28 (2008); 1613–1621.
- [7] OT Johnson, I Sigalas, EN Ogunmuyiwa, HJ Kleebe, MM Muller, and M Herrmann. Boron suboxide materials with Co sintering additives, Ceramics International, 36, (2010); 1767–1771.
- [8] OT Johnson, EN Ogunmuyiwa, I Sigalas, and M Herrmann. Boron suboxide materials with rare-earth metal oxide additives, In: Proceedings of International Conference on Manufacturing Engineering and Engineering Management Chemical Engineering and Technology, ICMEEM, WCE 2013, London, United Kingdom, 3–5 July, 2013.
- [9] C Ellison-Hayashi, M Zandi, D Shetty, P Kuo, R Yeckley, and F Csillag. Boron suboxide materials and method for its preparation. US Patent 5,330,937 (1994).
- [10] M Olofsson and T Lundström. Synthesis and structure of non-stoichiometric B<sub>6</sub>O. Journal of Alloys and Compounds, 257 (1997); 91–95.
- [11] CE Holcombe, JH Ottis, and O Horne. Method for preparing boron suboxide. US Patent 3,660,031 (1972).
- [12] X Lui, X Zhao, W Hou, and W Su. A new route for the synthesis of boron suboxide B<sub>7</sub>O. Journal of Alloys and Compounds, 223 (1995); L7 – L9.
- [13] IO Kayhan and OT Inal. Synthesis of aluminium infiltrated boron suboxide drag cutters and drill bits. Journal of Materials Science, 34 (1999); 4105–4120.
- [14] C Brodhag and F Thévenot. Hot pressing of boron suboxide B<sub>12</sub>O<sub>2</sub>. Journal of Less Common Metals, 117 (1986); 1–6.
- [15] BF Goosey. Method of fabricating boron suboxide articles. US Patent 3,816,586,A (1974).
- [16] DR Petrak, R Robert, and GR Atkins. Mechanical properties of hot-pressed boron suboxide and boron. Ceramics Society Bulletin, 53 (1974); 569–573.
- [17] F Sevim, F Demir, M Bilen, and H Okur. Kinetic analysis of thermal decomposition of boric acid from thermogravimetric data. Korean Journal of Chemical Engineering, 23(5) (2006); 736 – 740.
- [18] H Hubert, LAJ Garvie, B Devouard, PR Buseck, WT Petuskey, and PF McMillan. High pressure high temperature synthesis and characterization of boron suboxide (B<sub>6</sub>O). Chemistry of Material, 10 (1998); 1530–1537.
- [19] H Hubert, LAJ Garvie, B Devouard, PR Buseck, WT Petuskey, and PF McMillan. High pressure high temperature synthesis of superhard alpha-rhombohedral boron-rich solids in B-C-N-O. Materials Research Society, symposium proceeding, 499 (1998); 315.
- [20] HJ Kleebe, S Lauterbach, TC Shabalala, M Herrmann, and I Sigalas. B<sub>6</sub>O: A correlation between mechanical properties and microstructure evolution upon Al<sub>2</sub>O<sub>3</sub> addition during hot-pressing. Journal of American Ceramics Society, 91 (2008); (2) 569–575.