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<td><strong>Author(s)</strong></td>
<td>Solodkyi, Levgen; Borodianska, Hanna; Zhao, Ting; Sakka, Yoshio; Badica, Petre; Vasylkiv, Oleg</td>
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B₆O ceramic by *in-situ* reactive spark plasma sintering of a B₂O₃ and B powder mixture

Ievgen SOLODKYI, Hanna BORODIANSKA, Ting ZHAO, Yoshio SAKKA, Petre BADICA and Oleg VASYLKIV

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Key-words : Boron suboxide (B₆O), Spark plasma sintering, In-situ route, Hardness, Fracture toughness

1. Introduction

Boron suboxide (B₆O) is a light weight material and has promising physical and chemical properties such as high hardness, high thermal conductivity, good chemical inertness, and excellent wear resistance. Physical properties are related to short interatomic bonding’s length and to strongly covalent character of B₆O. The average hardness of 45 GPa and a fracture toughness of 4.5 MPa.m¹/² were measured on B₆O single crystals. These relatively high values recommend B₆O as a promising candidate to replace diamond and cubic boron nitride (cBN) based materials for different applications. Unlike both diamond and cBN that are obtained under high pressure synthesis conditions, synthesis of boron suboxide can be successfully performed under ambient pressure. However, a pure material with a high crystal quality and high oxygen doping level (i.e. x = 1 in B₆Oₓ) is difficult to fabricate by ambient pressure methods in contrast to more successful high pressure methods. Olofsson and Lundstrom showed that a higher oxygen content for synthesis under ambient pressure is obtained for a lower synthesis temperature. Apart from the problems addressed in the previous paragraph with phase purity and quality, B₂O₃ is also a difficult-to-sinter material. Pressure assisted methods under moderate pressures (usually less than 100 MPa) such as hot pressing (HP), and spark plasma sintering (SPS) were applied to obtain dense samples. In all these situations, B₂O₃ powders were used and they were prepared before sintering, i.e. processing was made in two separate steps (ex-situ route). In this work we propose and demonstrate formation in one processing step (in-situ route) of dense single phase B₆O ceramic of good quality by reactive SPS applied on mixtures of B₂O₃ and amorphous boron (aB). The choice for SPS is not trivial. Several reports indicate that owing to unconventional activation effects (such as formation of sparks accompanied by debatable plasma states, occurrence of hot spots, electrone diffusion and heating from inside to outside as in microwave sintering) induced by the use of pulsed currents for the sample heating in the SPS technique, sintering towards high density or completion of reactions can occur faster and at lower processing temperatures than for the conventional methods such as traditional sintering or HP. We also note higher flexibility of SPS versus HP in using high heating and cooling rates. Flexibility, lower processing temperatures and short processing times of SPS are advantages used for successful reactive SPS of B₂O₃ dense ceramic starting from a mixture of B₂O₃ and aB powders. This innovative *in-situ* approach generates a B₂O₃ ceramic with a good level of crystal quality, oxygenation and mechanical properties close to those of the best reported bulk samples obtained until now by ex-situ methods.

2. Experimental details

Commercial powders of B₂O₃ (99.0%, Kanto Chemical, Japan) and amorphous B (aB, 97%, International Laboratory) were the precursor powders. The B₂O₃ was dissolved in water and solvated with aB. Mole ratio was B₂O₃:aB = 1:1.4. After drying at 70°C the resulting powder mixture was loaded into a graphite mould system with punches. Sample diameter is 1 cm. A Ta-foil was used to effectively avoid the contact between the powder mixture and graphite. The mould system containing the powder mixture was placed into a SPS furnace (“Dr. Sinter” SPS-Synx 1050, Japan). Heating up to 1200 or 1250°C was performed with a heating rate of 400°C/min. The high heating rate was selected to suppress strong melting before reaching
stability domain of $B_6O$ and possible evaporation of $B_2O_3$. According to Dacic et al.,$^{17}$ $B_2O_3$ in air atmosphere and under normal conditions is up to 1600°C in the liquid state and above this temperature is in the gas state. In our SPS experiments we used Ar-flow. A uniaxial pressure of about 30 MPa was applied at room temperature on the punches of the mould system in order to ensure a good electrical stability during SPS processing. Three sets of SPS experiments were performed:

(i) Low temperature in-situ reactive SPS: powder mixture was SPSed at 1200 or 1250°C for 15 or 30 min.

(ii) High temperature ex-situ SPS-optimum sample obtained at point (i) was reheated by SPS up to 1800°C. The heating rate was 110°C/min and the dwell time was 1 min. The uniaxial pressure of 80 MPa was applied gradually.

(iii) One step (two-temperature) in-situ reactive SPS-optimum conditions determined from experiments (i) and those from (ii) were applied in a single SPS run. Namely, SPS heating was up to 1250°C at a constant uniaxial pressure of 30 MPa and after a dwell time of 30 min heating continued up to 1600–1800°C with a heating rate of 110°C/min, while the uniaxial pressure was gradually increased from 30 to 80 MPa.

In all SPS experiments cooling was performed with 100°C/min down to 600°C.

The density of the samples was measured by Archimedes method in ethanol.

X-ray diffraction (XRD) patterns were taken with Rigaku Ultima IV (Japan) diffractometer (Cu Kα radiation). The software used for the structural Rietveld refinements was PDXL (version 2.0.3.0, Rigaku Corporation). The microstructure of the samples was visualized using a scanning electron microscope (JEOL JSM 7001F, Japan). High density bulk SPSed samples were polished and electrochemically etched in 1% KOH water solution for 30 s at 3.5 V.

Vickers hardness ($HV_{9.8N}$) was measured by indentation technique using a microhardness tester (MHV1000, China). A load of 9.8 N (1 kg load) was applied on the polished surface of the samples for a holding time of 10 s. Average values of $HV_{9.8N}$ were calculated for at least 5 measurements per sample. Fracture toughness was determined according to Niihara et al.$^{18}$

$$K_{IC} = 9.052 \times 10^{-3} (HV)^{3/2} (Y/2D)^{1/2}$$

where $HV$ is Vickers hardness, $Y$ is Young’s modulus, $d$ is the average diagonal line length of the indentation print, and $I$ is the average length of the cracks.

3. Results and discussion

3.1 Low temperature in-situ reactive SPS

In our previous work$^{10}$ we obtained $B_6O$ ceramic by ex-situ Spark Plasma Sintering. In the first step, a suboxide $B_4O$ powder was synthesized through the reaction of $B_2O_3$ and $aB$ at a temperature of 1300°C for 2 h and in an electrical furnace. In the second step, $B_2O_3$ powder after an intermediate washing to remove residual $B_2O_3$ and subsequent drying was SPSed in Ar at 1800°C. When the uniaxial SPS pressure was 80 MPa, sample attained high values of Vickers hardness and fracture toughness of 34.8 ± 1.1 GPa and 4.0 ± 0.1 MPam$^{1/2}$, respectively.

Based on these results, in this work we attempted in-situ reactive SPS of the $B_2O_3$ and $aB$ powder mixture at 1300°C for 2 h. These SPS conditions were similar to those applied in the first step of the ex-situ route when conventional heating was performed. However, samples processed by in-situ SPS have shown poor quality consisting of $B$, $B_2O_3$ and traces of $B_6O$. The identified problem was evaporation of $B_2O_3$ before full reaction with $aB$ to form $B_6O$. We decided to lower SPS temperature and dwell time. XRD patterns of the samples SPSed at 1200 and 1250°C for 15 or 30 min are presented in Fig. 1. A high purity $B_6O$ sample is obtained for the optimum SPS processing at 1250°C and for 30 min. It is noteworthy that lower temperatures and times are necessary during spark-plasma-sintering than in the case of conventional processing. On the other hand, Dacic et al.$^{17}$ for conventional heating in air atmosphere indicated a higher temperature of 1600°C for the $B_2O_3$ evaporation. Olofsson and Lundstrom$^{19}$ noted that for a mixture of $aB$ and $B_2O_3$ conventionally heated at temperature of 1450°C for long heating time of 100 h was necessary to remove amorphous phase observed in XRD and ascribed to residual $B_2O_3$. In addition, Olofsson and Lundstrom$^{19}$ found that, when using mixtures of crystalline $a$-boron and $B_2O_3$, amorphous phase was not present. Moisture content was also shown to influence reactions and evaporation involving $B_2O_3$.$^{19}$ Considering the above observations, in our case it is probable that different quality of the raw powders and of their mixture when compared with literature and also specific unconventional features of SPS mentioned in Introduction are responsible for the observed effects.

For the sample SPSed at 1250°C for 30 min showing the highest $B_6O$ phase purity, XRD pattern was refined by Rietveld analysis (Fig. 2, Table 1). Structure refinement is based on space group R3m, No. 166, according to powder diffraction file (ICSD file 61512) with boron in position 18h and oxygen in position 6c (hexagonal axes). Some discrepancy in the lines intensity matching can be observed. This is due to the presence of residual amorphous phase (detectable especially as an enhanced background broad peak in the range of 2θ = 18–24°). Other works also observed amorphous residual phase.$^{19}$ Special care and corrections related to background extraction were not required and refinement software had the ability to overcome this problem so that calculated model fits well experimental data (Fig. 2). The lattice parameters of the $B_6O$ and reliability indices $R$ are given in Table 1.

Our results demonstrate a relatively high oxygen doping level (or occupancy in this particular case), i.e. $x = 0.89(99)$. In literature, for conventional processing at ambient pressure and for significantly longer reaction times at temperatures between 1250 and 1500°C values of $x$ between 0.76(6) and 0.93(8)$^{18,20}$ were reported (Fig. 3). The decrease of processing time and temperature while oxygen doping of $B_6O$ is at high level is of much interest. On the one hand, this is convenient from a technological
and economical perspective, and, on the other hand, can provide the background for fabrication of a B$_6$O ceramic with maximized mechanical properties. This is because a higher $x$ is required for higher mechanical properties owing to favorable situation towards easy formation of twins.\(^7\) A lower temperature and a shorter processing time can suppress growth of the particles. The decrease of particle size and enhancement of the amount of the grain boundaries can promote enhancement of the mechanical properties through the Hall & Petch effect.\(^{21,22}\)

### 3.2 High temperature ex-situ SPS

A SEM image of the sample in-situ SPSed for the optimum conditions of 1250°C for 30 min is presented in Fig. 4. Although low temperature in-situ SPS experiments were successful in obtaining single phase B$_6$O samples have shown low relative density (68%). Therefore, we performed ex-situ SPS of the sample already in-situ reactively SPSed at low temperature of 1250°C for 30 min. SPS conditions were selected to be the same as for the best sample from our previous work\(^\text{10}\) when B$_6$O phase was obtained before SPS by conventional synthesis (1300°C for 2 h). Note that in the present work no washing of the B$_6$O was performed between the first step of low temperature reactive SPS and the second step of high temperature SPS. The particle size in the in-situ SPSed sample (1250°C for 30 min) is below 500 nm and it is lower than the size (<1 µm) of the B$_6$O powder synthesized by conventional heating at 1300°C for 2 h presented in Ref.\(^{10}\)

Mechanical properties, density, and morphology after high temperature SPS (at 1800°C for 1 min with a heating rate of 110°C/min, and under a maximum uniaxial pressure of 80 MPa) on the samples already reacted by conventional heating (at 1300°C for 2 h) or by in-situ low temperature SPS (at 1250°C for 30 min) are shown in Table 2 and Fig. 5 (samples denoted Reference and Ex-situ 1800). Bulk samples show comparable density, mechanical properties, and morphology. The density is high and we also observe that samples have a high level $HV_{9.8N}$ and $K_{IC}$ (see also Section 3.3).

### 3.3 One step (two-temperature) in-situ reactive SPS

The results from Section 3.2 showed that washing between the two SPS steps of the powder obtained by in-situ low temperature reactive SPS is not critical. They also demonstrated that conditions of SPS applied on a powder synthesized by a conventional route are working for sintering of the sample reacted by low-temperature in-situ reactive SPS. These results were used to design the regime of one step (two-temperature) in-situ reactive SPS. Namely, B$_2$O$_3$ and aB powder mixture was heated up to 1250°C using conditions from the in-situ low temperature reactive SPS (400°C/min and under constant uniaxial pressure of 30 MPa), and, after a dwell time of 30 min, SPS heating continued with a heating rate of 110°C/min up to 1800°C, while uniaxial pressure was gradually increased to 80 MPa (from 30 MPa) following the same idea as in the high temperature ex-situ SPS. It is remarkable that this approach generates samples with a high density, $HV$ and

![Fig. 2. Rietveld refinement of the XRD pattern for B$_6$O sample synthesized by low temperature in-situ SPS at 1250°C for 30 min.](image1)

![Fig. 3. Comparative results of oxygen site occupancy as a function of reaction temperature for different B$_6$O samples. Reaction time is indicated. Samples from Ref. 9) heated at 1250 and 1350°C were obtained from a mixture of crystalline $\alpha$-boron and B$_2$O$_3$, while the other samples were synthesized from aB and B$_2$O$_3$ mixture. Samples from Ref. 20) were obtained from aB and ZnO powder mixtures. Conventional heating was used in Refs. 9) and 20).](image2)

![Fig. 4. SEM image of the B$_6$O sample after low temperature in-situ SPS processing at 1250°C for 30 min.](image3)

**Table 1.** Atomic coordinates, site occupancy, hexagonal lattice constants, and R-factors obtained by Rietveld refinement of B$_6$O$_2$ sample synthesized by in-situ SPS at 1250°C for 30 min.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$R_{wp}$ (%)</th>
<th>$R_p$ (%)</th>
<th>$R_B$ (%)</th>
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<tr>
<td>B(1)</td>
<td>18 h</td>
<td>0.1590(03)</td>
<td>0.8410(02)</td>
<td>0.6414(01)</td>
<td>1$^a$</td>
<td>3.38</td>
<td>5.72</td>
<td>5.362(13)</td>
<td>8.91</td>
<td>2.161</td>
</tr>
<tr>
<td>B(2)</td>
<td>18 h</td>
<td>0.1159(54)</td>
<td>0.8840(53)</td>
<td>0.8830(02)</td>
<td>1$^a$</td>
<td>3.38</td>
<td>5.72</td>
<td>5.362(13)</td>
<td>8.91</td>
<td>2.161</td>
</tr>
<tr>
<td>O</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.3735(04)</td>
<td>0.89(99)</td>
<td>3.38</td>
<td>5.72</td>
<td>12.354(42)</td>
<td>2.161</td>
<td>2.161</td>
</tr>
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</table>

$^a$not varied, $^bR_{wp}$ = weighted profile factor, $^cR_p$ = profile factor, $^dR_B$ = Bragg factor.
Table 2. SPSed samples, processing route, relative density (ρ), Vickers hardness $HV_{0.05N}$, and fracture toughness $K_{ic}$. (Theoretical density was taken 2.62 g/cm$^3$ for B$_6$O with full oxygen occupancy$^{20}$).

<table>
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<tr>
<th>Sample</th>
<th>Route</th>
<th>ρ (%)</th>
<th>$HV_{0.05N}$ (GPa)</th>
<th>$K_{ic}$ (MPa.m$^{1/2}$)</th>
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<tr>
<td>Reference$^{(b)}$</td>
<td>Ex-situ SPS, step 1: conventional heating (1300°C, 2 h)</td>
<td>98.3</td>
<td>34.7 ± 0.9</td>
<td>4</td>
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<tr>
<td>Ex-situ 1800</td>
<td>Ex-situ SPS, step 1: SPS heating (1250°C, 30 min) step 2: SPS reheating (1800°C, 1 min)</td>
<td>98.5</td>
<td>35.6 ± 0.9</td>
<td>4.1</td>
</tr>
<tr>
<td>In-situ 1800</td>
<td>In-situ SPS (one step), Reactive SPS heating (1250°C, 30 min + 1800°C, 1 min)</td>
<td>98.7</td>
<td>36.7 ± 1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>In-situ 1750</td>
<td>In-situ SPS (one step), Reactive SPS heating (1250°C, 30 min + 1750°C, 1 min)</td>
<td>98.5</td>
<td>36.3 ± 1</td>
<td>4.2</td>
</tr>
<tr>
<td>In-situ 1700</td>
<td>In-situ SPS (one step), Reactive SPS heating (1250°C, 30 min + 1700°C, 1 min)</td>
<td>97.1</td>
<td>33.6 ± 1.1</td>
<td>4.3</td>
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<tr>
<td>In-situ 1650</td>
<td>In-situ SPS (one step), Reactive SPS heating (1250°C, 30 min + 1650°C, 1 min)</td>
<td>93.6</td>
<td>31.1 ± 0.8</td>
<td>4.3</td>
</tr>
<tr>
<td>In-situ 1600</td>
<td>In-situ SPS (one step), Reactive SPS heating (1250°C, 30 min + 1600°C, 1 min)</td>
<td>89.7</td>
<td>28.3 ± 1</td>
<td>3.8</td>
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Fig. 5. SEM images of samples after SPS. Sample names correspond to Table 2.

Many brittle and hard ceramics. For single crystals of B$_6$O, $HV_{1.0N}$ and $K_{ic}$ were 46 GPa and 4.5 MPa.m$^{1/2}$. Crystalline surface of the crystals on which measurements were done was not identified. The reason why washing of the B$_6$O samples is not mandatory is that residual B$_2$O$_3$ removes through evaporation at high temperature SPS. In fact during SPS there might occur opposite effects of the gas squeezing depending on temperature and the applied SPS pressure and the gas trapping owing to sintering of the particles. Trapped gas hinders sintering making difficult achievement of density values close to theoretical ones. A possible advantage of SPS over the conventional heating is that SPS heating may not be only from outside to inside as for the samples subject to sintering in conventional furnaces, but can also have a component of heating from inside to outside as for microwave sintering as a consequence of pulsed current use$^{16}$. This can provide a different sintering uniformity pattern influencing gas release-trapping process. Another problem is that as resulting B$_6$O ceramic SPSed at 1800°C (in-situ or ex-situ) consists of large grains. To enhance the fracture toughness, introduction of interfaces into bulk ceramic is recognized as a powerful method. In this regard two approaches can be applied: (i) to increase the number of grain boundaries by decreasing the grain size and (ii) to introduce interfaces by means of a secondary phase such as B$_2$O$_3$ in B$_6$O i.e. to obtain a composite. Considering assumptions and observations from this paragraph it is meaningful to look for the optimization of the SPS conditions aiming especially higher fracture toughness, i.e. to obtain a less brittle material with potential for practical applications. In this work the maximum temperature in the one step (two-temperature) in-situ reactive SPS was lowered to values of 1750, 1700, 1650 and 1600°C. Above 1250°C and after a dwell time of 30 min (as before), SPS conditions were: heating rate of 110°C/min, maximum uniaxial pressure of 80 MPa (gradually applied), dwell time at maximum temperature of 1 min. Relative density, $HV_{0.05N}$ and $K_{ic}$ are gathered in Table 2. Relative density and $HV_{0.05N}$ are decreasing with the decrease of maximum SPS temperature, but $K_{ic}$ is almost constant (4.2–4.3 MPa.m$^{1/2}$) for SPS maximum temperature of 1650–1800°C. At the same time, samples SPSed at a lower maximum temperature consist of smaller grains (e.g. compare sample obtained by in-situ two-temperature SPS for a maximum temperature of 1800°C with...
sample obtained at 1750°C, Fig. 5). Expectations were that if a lower grain size is obtained for high density samples (SPSed at 1700, 1750 or 1800°C), a higher $K_{IC}$ is attained. The observed inconsistency suggests opposite processes possibly related as anticipated to behavior of the $B_2O_3$ residual phase, to the oxygen doping and stability of the main $B_6O$ phase and to the morphology evolution during SPS. More research on details of morphology, phase and composition evolution and on SPS optimization experiments are required to understand the details and to explain and possibly to enhance the mechanical properties of the $B_6O$ ceramic.

4. Conclusions

One step in-situ two-temperature reactive SPS (applied on $B_2O_3$ and $aB$ powder mixture with mole ratio 1:14) is proposed. It is shown that this route allows fabrication of $B_6O$ bulk ceramic with a relative density above 98% that shows Vickers hardness of 36.7 ± 1.2 GPa and fracture toughness of $K_{IC} = 4.2 ± 0.15$ MPa.m$^{1/2}$. These values are comparable with the best values reported in literature for ex-situ methods (conventional or by SPS) pure and added $B_6O$ polycrystalline materials.

References