

High temperature properties of B₆O-materials

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Abstract

B₆O is a potential superhard material with a hardness of 45 GPa measured on single crystals. Recently it was found that different oxides can be utilized as an effective sintering additive which allows densification under low pressures. In this work the effect of addition of Y₂O₃/Al₂O₃ on high temperature properties was investigated using impulse excitation technique (IET), hardness measurements and dilatometric measurements. The IET technique reveals the softening of the residual B₂O₃ in the materials without additives at 450 °C; in the materials with Y₂O₃/Al₂O₃ the softening is observed at only about 800 °C. This data agrees with the values found for different borate glasses.

The materials showed no pronounced reduction of hardness at these temperatures. This is additional evidence, supporting previous observations that the material consists of pure grain boundaries between B₆O grains. Hardness values (HV5) of up to 17 GPa at 1000 °C were observed.

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1. Introduction

B₆O-based materials are known as one of the hardest materials after diamond and cubic boron nitride or its solid solutions like BC₂N with a hardness of 45 GPa measured on single crystals.^{1–3} However, in contrast to these promising properties, B₆O materials have not yet found commercial applications, because full densification requires high pressures (1–5 GPa).⁴ The materials densified at high pressures have good hardness but a very low fracture toughness of 1–2 MPa m^{0.5}.

Efforts have been made to enhance the fracture toughness of B₆O by forming B₆O composites with other hard materials such as diamond, boron carbide and cBN. These efforts result in high hardness values but still low fracture toughness values < 1.8 MPa m^{0.5}.^{5–7}

B₆O materials were prepared by hot pressing of mixtures of B and B₂O₃ at temperatures up to 2000 °C.^{8,9} These materials had

high microhardness, but no other mechanical properties were determined. Hot pressing of B₆O powders in a wide temperature range described by C. Brodhag et al. resulted only in porous materials.¹⁰

Recently it was reported that B₆O can be hot pressed or densified by SPS with oxide additions. The resulting materials showed improved fracture toughness with a slight reduction in hardness, as compared to pure B₆O materials.^{11–15}

Microstructural investigations have shown that the oxide additives form an amorphous grain boundary containing beside Y₂O₃, Al₂O₃ as well as B₂O₃. The amorphous oxide phases are mostly concentrated in the triple junctions. Most of the grain boundaries are not wetted by the additives.¹⁵ The same behaviour was found for the B₂O₃ phase in the pure B₆O.¹² It is expected that beside B₆O the additional phases formed will have an influence on the high temperature behaviour of the materials. Recently it was found the additives have an influence on the oxidation behaviour of B₆O materials.¹⁶

Elastic constants of B₆O materials were measured to lie in the range of 485–440 GPa for pure B₆O materials. Increasing additive content reduces the *E*-modulus slightly.¹⁷

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Table 1
Composition, hardness and thermal expansion coefficient (RT–1000 °C) of the B₆O-materials prepared and analyzed.

Composition wt%		Additive content vol%	Density g/cm ³	Density %theor. density	HV0.4 GPa	HV5 GPa	Thermal expansion coefficient (1000 °C) 10 ⁻⁶ /K
B6O-pure	B ₆ O	0	2.47	97	35.5 ± 0.8	27.2 ± 0.8	5.6 ± 0.2
B6O–AlYO2.3	B ₆ O/3.8% Y ₂ O ₃ /Al ₂ O ₃	2.3	2.62	>99	33.0 ± 0.6	25.2 ± 0.3	–
B6O–AlYO2.6	B ₆ O/4.6% Y ₂ O ₃ /Al ₂ O ₃	2.6	2.59	>99	–	25.6 ± 0.2	6.2 ± 0.2
B6O–AlYO7.9	B ₆ O/12.7% Y ₂ O ₃ /Al ₂ O ₃	7.9	2.62	97	31.1 ± 0.3	21.2 ± 0.9	–

There are no data available concerning the high temperature hardness and elastic constants of B₆O materials. Therefore the aim of this work was to investigate the elastic properties and hardness of B₆O materials at high temperatures and to discuss it in relation to the microstructure.

2. Experimental

2.1. Preparation of the materials

The starting B₆O-powder was produced in laboratory scale as described elsewhere.¹⁴ The chemical composition of the B₆O powder was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6000, THERMO SCIENTIFIC, USA). The following cation impurities were determined: Fe = 0.081 wt%, Cr = 0.077 wt%, Al = 0.047 wt% and Mg = 0.12 wt%. The mean particle size of the starting powder was 0.5 μm. The powders used beside B₆O were Al₂O₃ (AKP50, SUMITOMO CHEMICAL, Japan) and Y₂O₃ (Grade C, H.C. STARCK, Germany). The oxygen stoichiometry of produced boron suboxide was not investigated in detail. But XRD measurements and measurements of the oxygen content in the starting powder indicate a composition of approximately B₆O_{0.8} and B₆O_{0.85}. The literature clearly points out that synthesis of nearly stoichiometric B₆O is only possible under high pressure conditions.⁸ At ambient pressure conditions compositions between B₆O_{0.72} and B₆O_{0.85} can be expected. Therefore our composition is near to the upper limit of the range. The powder mixing was carried out in an attrition mill (PE075, Netzsch company, Germany) with ethanol as solvent and alumina milling balls (1–2 mm, 99.6% pure Al₂O₃). After milling, the suspension was dried using a rotavap.

FAST/SPS was carried out on a HP D25 furnace (FCT, Germany) using graphite dies and graphite foils. The graphite foils were coated with a BN suspension to prevent a chemical reaction between the sample and the graphite die/foil. Densification was carried out in argon and the temperature measurement was performed with a standard pyrometer in the centre of the die. The heating rate was 50 K/min. The diameter of the samples was 60 mm.

Two sets of materials were densified. A pure B₆O material was prepared at 1850 °C and 50 MPa. The resulting density was 2.47 g/cm³, which corresponds to 97% of theoretical density.

A second set of materials was prepared by adding different amounts of Y₂O₃/Al₂O₃ additives at 1850 °C for 5 min. The compositions and properties are given in Table 1.

2.2. Materials characterization

Before characterization all sample surfaces were sand blasted to remove h-BN and some formed B₄C material adhering to the sample and then cut and ground into the required size.

Cross sections of the materials were polished and analyzed with a field-emission scanning electron microscope (FESEM, ULTRA 55, CARL ZEISS AG, Germany) with energy-dispersive X-ray spectroscopy system (EDS, Oxford Instruments, UK) attached to it. Additionally plasma etching was carried out using CF₄ gas. The phase composition was determined by X-ray diffraction (XRD, GE Inspection Technologies, Germany, Cu Kα).

The elastic modulus (*E*) and damping (*Q*⁻¹) of different grades of B₆O as a function of temperature were measured using the impulse excitation technique (IET). Specimen support, impulse location and signal pickup points are selected to induce and measure specific modes of vibration. Carbon wire was used for the sample suspension inside the furnace. Details about the equipment and technique can be found in the literature.^{18,19} All the measurements were performed in argon from room temperature up to 1200 °C. During the consecutive thermal cycle, samples were repeatedly heated up to different temperatures 500, 800 and 1200 °C. Heating and cooling rate were kept constant (2 K/min) for all the measurements.

For microhardness testing, a MHT-10 apparatus with Vickers indenter (Anton Paar, Austria) was used. The indentation was held at the highest load for 10 s. Five indentations were made for every material and every load. The high temperature hardness (HV5) was determined in an apparatus developed together with Hegewald & Peschke (Germany) which can measure the hardness up to 1500 °C in vacuum. The indentation was held at the highest load for 10 s. Five indentations were made for every material and every load.

The thermal expansion of the materials was measured from room temperature up to 850 °C (pure material) or 1000 °C (B6OAlYO2.6) with a heating rate of 2 K/min in argon using TMA 402 (Fa. Netzsch, Germany). The sample size was 3 mm × 3 mm × 20 mm.

3. Results

The densities of the materials given in Table 1 reveal that the samples with the oxide additives are nearly fully dense, while the pure B₆O material contains somewhat higher residual porosity than the oxide containing samples. The microhardness values of

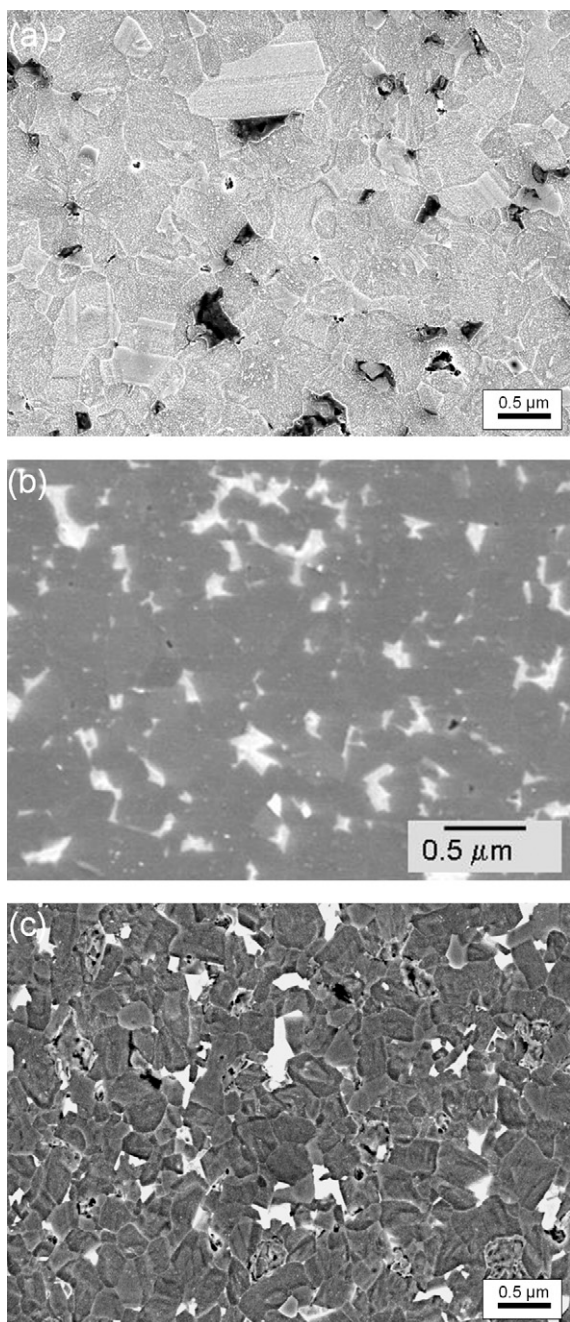


Fig. 1. SEM micrographs of the pure B₆O-material (a) and the B₆O-material containing oxide additives (B₆O–AlYO2.3) (b and c) after IET measurement; the samples (a) and (c) were plasma etched. The bright phase in the figures (b) and (c) represents triple junctions filled with the oxide additives.

the materials are in the range of 32–37 GPa. Similar values were reported for these types of materials previously.^{11–15,17}

The microstructure analysis showed that the grain size in the pure B₆O material and the material containing the additives is in the range of 0.1–2 μm. The B₆O grains often show euhedral morphology. Partially stacking faults or twinning planes are visible. The microstructure reminds the microstructures found for dense materials produced under high pressure.^{7,27} The oxide additives form distinct triple junctions (Fig. 1). XRD measure-

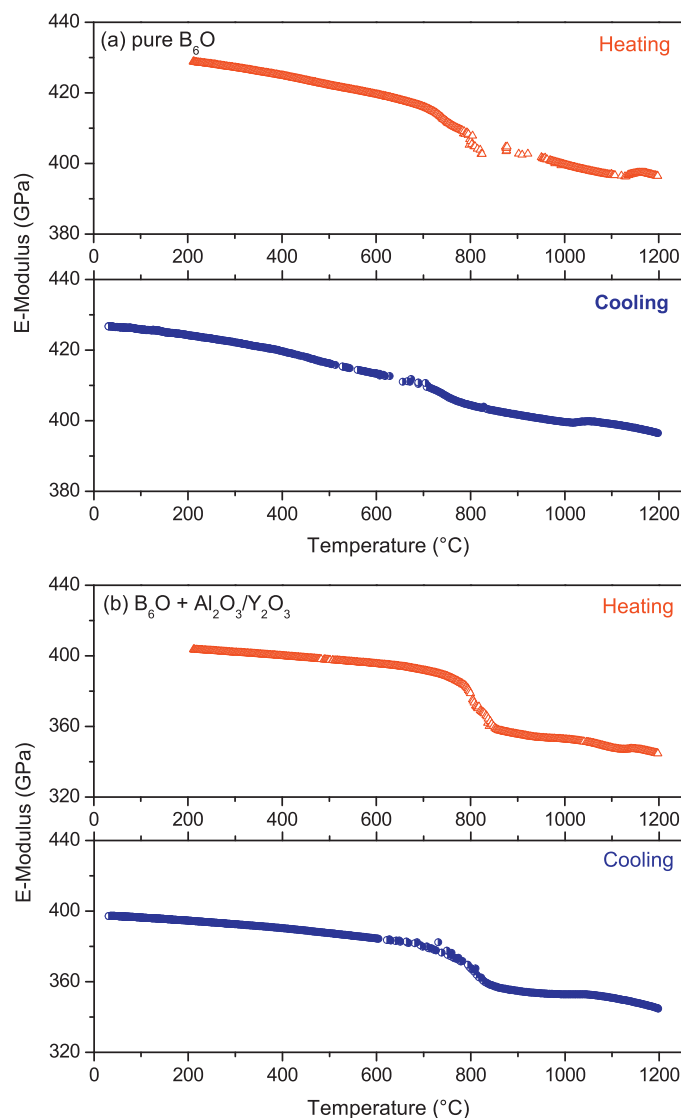


Fig. 2. Temperature dependence of the *E*-modulus of the pure B₆O-material (a) and the material B₆O–AlYO2.3 containing Y₂O₃/Al₂O₃ additives (b).

ments reveal no crystalline phases beside B₆O in all materials (Fig. 5).

The *E*-modulus and the damping determined by the impulse excitation technique as a function of temperature are given in Figs. 2 and 3. Table 2 summarizes the damping peaks present in the samples. Decreases in *E*-modulus were observed after the complete thermal cycling of up to 1200 °C for both materials. After the measurement, the *E*-modulus dropped by 4.5% and 7.5% for the pure B₆O-material and the material containing oxide additives (B₆O–AlYO2.3), respectively.

For the pure B₆O-material two damping peaks located at 450 °C (P1) and 745 °C (P2), respectively, were observed during the thermal cycles.

In the B₆O material containing 2.3 vol% Al₂O₃/Y₂O₃ additives (B₆O–AlYO2.3) two peaks are observed. Peak P2' at 805 °C is in a similar range as in the pure material and another partially overlapping peak P3' was observed at 840 °C. During cooling this last peak disappears.

Table 2
Temperatures of various observed damping peaks in the pure B₆O-material and the material with oxide additives (B6O–AlYO2.3).

Sample	Peak No	Cycle 1 (T_{\max} 500 °C)		Cycle 2 (T_{\max} 800 °C)		Cycle 3 (T_{\max} 1200 °C)	
		Heating	Cooling	Heating	Cooling	Heating	Cooling
Pure B ₆ O	P1	445 °C	450 °C	445 °C	450 °C	445 °C	450 °C
	P2			740 °C	745 °C	740 °C	745 °C
B ₆ O with Y ₂ O ₃ /Al ₂ O ₃	P2'					805 °C	810 °C ^a
	P3'					840 °C	–

^a Not clear (difficult to discern).

The dependence of the hardness on temperature is given in Fig. 4. The thermal expansion dL/L_0 of pure B₆O-material measured up to 850 °C is 0.50% (extrapolated value for 1000 °C: 0.56%). For the additive containing material the expansion is slightly higher and a value of 0.60% at 1000 °C was obtained (Table 1).

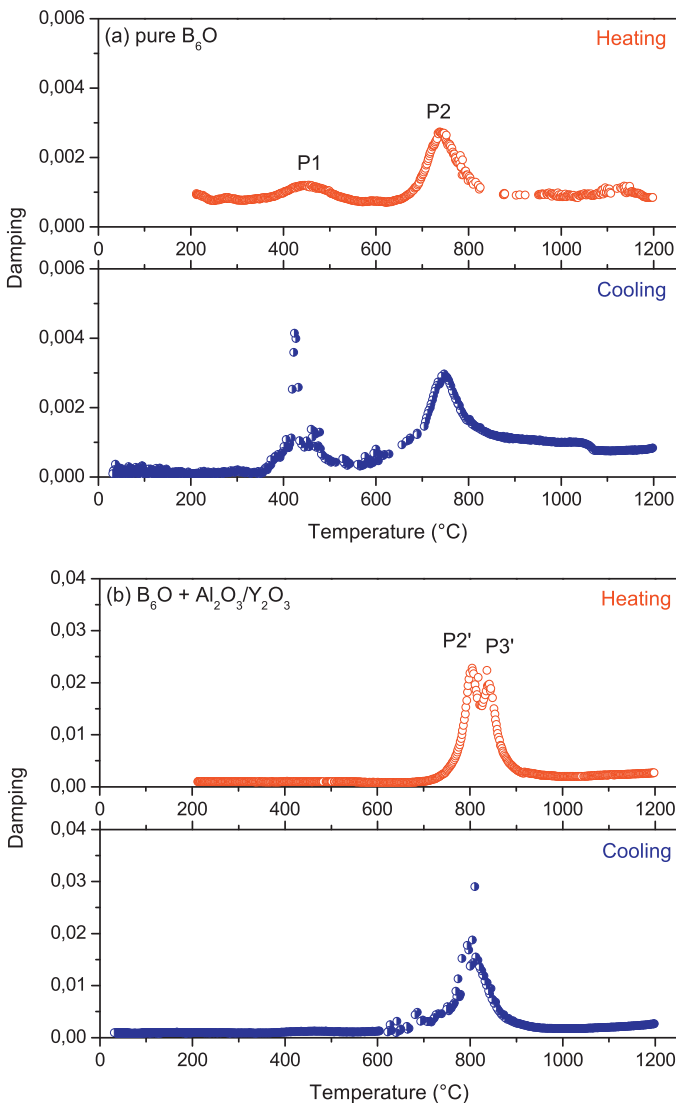


Fig. 3. Temperature dependence of the damping of the pure B₆O-material (a) and the material B6O–AlYO2.3 containing Y₂O₃/Al₂O₃ additives (b).

4. Discussion

The polished cross sections of the pure B₆O material showed that the material consists of B₆O grains in the range of 0.1–1.5 μm. The residual B₂O₃ is not visible because it is pulled out from the sample surface while polishing due to its low chemical stability. Therefore in places where B₂O₃ was located before polishing only pores are left over. From the starting powder it can be estimated that the B₂O₃ content must be less than 2 wt%. B₂O₃ also decomposes partially during sintering,¹¹ therefore the real volume fraction would be less than 2 vol%. The TEM investigations of pure B₆O showed that the remaining B₂O₃ is only localized as amorphous phase in the triple junctions. No wetting of the grain boundaries by B₂O₃ took place.¹² The starting B₆O materials contain some aluminium and magnesium (Al = 0.05 wt% and Mg = 0.12 wt%). The microstructural analysis showed that these impurities form very few amorphous triple junctions in the material. Based on these microstructural observations the damping peaks of the pure B₆O can be interpreted. It is known that the B₂O₃ glasses have a transition temperature in the range 450–500 °C.²⁰ This is the same temperature range in which also the first damping peak was observed. Thus this peak can be attributed to the softening of the amorphous B₂O₃ triple junctions.

The second peak is most probably connected with the softening of the MgO/Al₂O₃/B₂O₃ containing triple junctions. Such glassy phase has glass transition temperatures in this tempera-

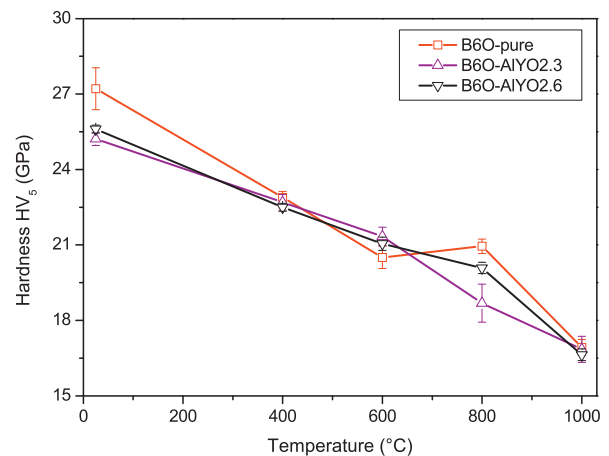


Fig. 4. High temperature hardness of B₆O materials with and without sintering additives.

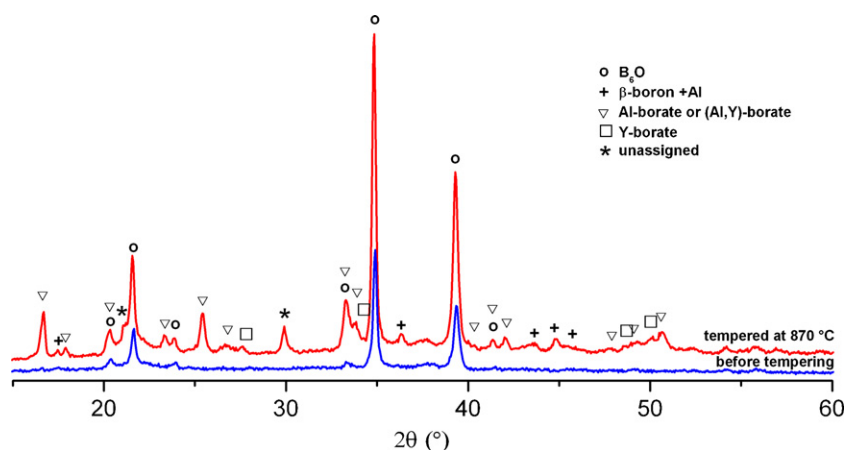


Fig. 5. Comparison of XRD data for high additive sample B6O–AlYO7.9 before and after tempering at 870 °C for 3 h in argon.

ture region.^{21,22} Therefore it is very likely that the P2 peak is connected with the softening of this phase. These amorphous triple junctions are stable up to 1200 °C since the peak is still present during cooling from that temperature.

The grain boundaries of the B₆O grains are not wetted by B₂O₃ or the oxide impurity containing amorphous phase. Additionally these inclusions have only a low volume fraction. Therefore the softening of these phases is visible neither in the elastic modulus (Fig. 2) nor in the thermal expansion.

The use of Al₂O₃/Y₂O₃ sintering aids (sample B6O–AlYO2.3; B6O–AlYO2.6) improves the densification of the materials significantly.^{13,15} The grain size in these materials is slightly higher than for the pure B₆O material. The microstructural analysis reveals that these additives form amorphous Al₂O₃/Y₂O₃/B₂O₃ containing triple junctions. This amorphous grain boundary phase is chemically much more stable than the B₂O₃ grain boundary phase in the pure B₆O material and therefore it is also stable during polishing. The triple junctions are visible as bright phases at the SEM images.

Additionally in the microstructure some boron rich inclusions were found containing B and approximately 3 at% of Al beside minor amounts of Mg as determined by EDX. TEM investigations of B₆O-materials with similar amount of oxide additions showed, that also in this case the grain boundary phases are not wetted, i.e., the triple junctions are isolated. No more B₂O₃ containing triple junctions were observed either.^{15,17}

In samples with higher amount of additives the boron rich phase could be determined by XRD as a β-boron structure,²³ which is known to incorporate some additional cations on the interstitial positions between the B₁₂-polyhedron.²⁴

Due to the nonexistence of B₂O₃-containing triple junctions in the material with the oxide additives the previously observed peak P1 at 440–450 °C observed in undoped B₆O sample has disappeared. This is an additional indirect proof for the interpretation of the peak. From the investigations of borate glasses it is known that the transition temperature increases up to 800 °C with Y₂O₃/Al₂O₃ addition.^{25,26} At this temperature the softening of the grain boundary in the oxide additive containing B₆O-materials has to be expected. By IET measurements a peak P2' at 805 °C was observed during heating and cooling.

Another partially overlapping peak P3' was found only during heating at 840 °C. A tentative interpretation of these observations is that the peak P2' corresponds to the reversible glass transition of the B₂O₃–Al₂O₃–Y₂O₃ triple junctions. The temperature corresponds to the values expected by the literature data for the glass transition temperature.^{25,26} The P3' peak which disappears during cooling corresponds to a process which is not reversible. A possible explanation could be partial crystallisation of the glassy triple junctions. In yttrium aluminium borate glass–ceramics crystallisation temperatures were observed in the range of 750–850 °C,²⁵ which fits the observed temperature for peak P3'.

A heat treatment of the materials B6O–AlYO2.3, B6O–AlYO2.6 and a material with higher additive content B6O–AlYO7.9 (7.9 vol% Al₂O₃/Y₂O₃ additives) at 870 °C in an argon atmosphere for 3 h resulted in crystallisation of the additive phase which could be detected by XRD in the materials B6O–AlYO2.6 and B6O–AlYO7.9. The crystalline phases formed could be mainly assigned to Al- and Y-borates. But not all peaks could be unequivocally explained by phases in the database (Fig. 5).

In the temperature range of the softening of the triple junctions also a reduction of the elastic constant during heating and again an increase during cooling was observed. This is in agreement with the interpretation of the damping peaks P'.

None of the investigated samples showed a special effect in the thermal expansion curves. This is most probably due to the low content of the additives and due to the non-wetting of the grain boundaries. Nevertheless the materials with the oxide additives showed a slightly higher thermal expansion (Table 1).

All the investigated materials, independently of the additive content showed a constant reduction in hardness between room temperature and 1000 °C. This could be explained by the fact that in these materials pure (non-wetted grain boundaries were observed. Therefore the softening of the grain boundaries will not reduce the stability of the three dimensional network of the B₆O grains. The reduction of hardness must primary be caused by the softening of the B₆O crystal structure or pure B₆O grain boundaries. Further investigation of this behaviour would be necessary. Nevertheless at 800 and 1000 °C the mate-

rials showed a higher hardness in comparison to the commercial DBC 50 material based on BN for which a hardness HV_5 of 15.5 ± 0.4 GPa at 1000°C was measured. Therefore the B_6O material could be a possible candidate for cutting applications.

5. Conclusions

The impulse excitation technique (IET) was used to characterise the softening of B_6O materials with and without sintering additives. The results are strongly in agreement with the microstructural observations, that the pure B_6O materials contain some isolated triple junctions filled with B_2O_3 . This secondary phase starts to soften at 445°C . But this has no remarkable influence on the hardness and the E -modulus. This is because the B_2O_3 content has only a low concentration (<2 vol%) and does not wet the grain boundaries between the B_6O -grains. A nearly monotonic reduction of the E -modulus with temperature was found. The IET-measurement also confirmed that the Mg- and Al-impurities (<0.2 wt%) of the starting B_6O -powder form mostly Mg–Al–borate glassy isolated triple junctions, which soften at 740 – 750°C .

The use of oxide additives (Al_2O_3/Y_2O_3) in B_6O materials prevents the formation of B_2O_3 -triple junctions. They mostly formed a Y–Al–borate phase, which softens at about 800°C . Although in these materials the grain boundaries are not wetted by the oxides a drop of the E -modulus of these materials was observed at these temperatures.

The drop in the high temperature hardness is similar for all investigated materials despite the existence of different amounts of soft glassy phases. The low influence of the amount of the grain boundary phases on the high temperature hardness could be caused by the pure boundaries between the B_6O grains which were observed in these materials. The reduction of the hardness must therefore primarily be connected with the crystal structure of the B_6O themselves or with the structure of the grain boundaries. Further investigations are necessary to understand the reasons and to use this knowledge for further optimizing the materials.

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References

1. He D, Zhao Y, Daemen L, Qian J, Shen TD, Zerda TW. Boron suboxide: as hard as cubic boron nitride. *Appl Phys Lett* 2002;**81**(4):643–5.
2. McMillan PF. Pressing on: the legacy of Percy W. Bridgman. *Nat Mater* 2005;**4**:715–8.
3. Nieto-Sanz D, Loubeyre P, Crichton W, Mezouar M. X-ray study of the synthesis of boron oxides at high pressure: phase diagram and equation of state. *Phys Rev B* 2004;**70**(21), 214108 6 pp.

4. Hubert H, Garvie LAJ, Devouard B, Buseck PR, Petuskey WT, McMillan PF. High-pressure, high-temperature synthesis and characterization of boron suboxide (B_6O). *Chem Mater* 1998;**10**:1530–7.
5. Sasai R, Fukatsu H, Kojima T, Itoh H. High pressure consolidation of B_6O -diamond mixtures. *J Mater Sci* 2001;**36**:5339–43.
6. Itoh H, Maekawa I, Iwahara H. Microstructure and mechanical properties of B_6O - B_4C sintered composites prepared under high pressure. *J Mater Sci* 2000;**35**:693–8.
7. Itoh H, Yamamoto R. B_6O -cBN composites prepared by high-pressure sintering. *J Am Ceram Soc* 2000;**83**:501–6.
8. Ellison-Hayashi C, Zandi C, Shetty DK, Kuo P, Yeckley R, Csillag F. Boron suboxide material and method for its preparation. US Patent 5,135,895; 1992.
9. Goosey BF, Anderson SC. Method of fabricating boron suboxide articles. US Patent 3,816,586; 1974.
10. Brodhag C, Thévenot CF. Hot pressing of boron suboxide $B_{12}O_2$. *J Less Common Met* 1986;**110**:1–6.
11. Andrews A, Herrmann M, Shabalala TC, Sigalas I. Liquid phase assisted hot pressing of boron suboxide materials. *J Eur Ceram Soc* 2008;**28**:1613–21.
12. Kleebe H-J, Lauterbach S, Shabalala TC, Herrmann M, Sigalas IJ. B_6O : a correlation between mechanical properties and microstructure evolution upon Al_2O_3 addition during hot-pressing. *J Am Ceram Soc* 2008;**91**(2):569–75.
13. Herrmann M, Raethel J, Bales A, Sempf K, Sigalas IJ, Hoehn M. Liquid phase assisted densification of superhard B_6O -materials. *J Eur Ceram Soc* 2009;**29**:2611–7.
14. Shabalala TC, Mclachlan DS, Sigalas IJ, Herrmann M. Hard and tough boron suboxide based composites. *Adv Sci Technol* 2006;**45**:1745–50.
15. Herrmann M, Kleebe H-J, Raethel J, Sempf K, Lauterbach S, Mueller M, et al. Field-assisted densification of superhard B_6O materials with Y_2O_3/Al_2O_3 addition. *J Am Ceram Soc* 2009;**92**:2368–72.
16. Herrmann M, Thiele M, Jaenicke-Roessler K, Freemantle CS, Sigalas I. Oxidation resistance of B_6O -materials with different additives. *J Eur Ceram Soc* 2011;**31**(9):1771–7.
17. Andrews A. Development of boron suboxide composites with improved toughness. PhD Thesis, Wits; 2008.
18. ASTM. *Standard test method for dynamic Young's modulus, shear modulus, and Poisson's ration by impulse excitation of vibration. C 1259-08*; 2008.
19. Roebben G, Bollen B, Brebels A, Van Humbeeck J, Van der Biest O. Impulse excitation apparatus to measure resonant frequency, elastic moduli and internal friction at room and high temperature. *Rev Sci Instrum* 1997;**68**:4511–5.
20. Scholze H. *Glass*. New York: Springer; 1990. p. 162.
21. Chenga Y, Xiao H, Shuguang C, Tang B. Structure and crystallization of B_2O_3 - Al_2O_3 - SiO_2 glasses. *Phys B: Condens Matter* 2009;**404**(8–11):1230–4.
22. Hamzawy EMA, Darwish H. Vitrification and devitrification phenomena in the ternary MgO- Al_2O_3 - B_2O_3 system". *Ceram Int* 2008;**34**(8):1965–9.
23. Thiele M, Herrmann M. Private communications.
24. Albert B, Hillebrecht H. Boron: elementary challenge for experimenters and theoreticians. *Angew Chem Int Ed* 2009;**48**:8640–68.
25. Applewhite AL, Day DE. *Proc XVth Intern Congr on Glass*. 1989. p. 337.
26. Hovhannisyanyan RM, Grigoryan BV, Alexanyan HA, Shirinyan Manuk HG, Poghosyan A, Petrosyan BV, et al. Glass formation and crystallisation behaviour of yttrium aluminium tetraborate glass-ceramics. *Glass Technol—Eur J Glass Sci Technol Part A* 2009;**50**(4):221–6.
27. Chen C, He D, Kou Z, Peng F, Yao L, Yu R, et al. B_6O -based composite to rival polycrystalline cubic boron nitride. *Adv Mater* 2007;**19**:4288–91.