Reactive sintering process and thermoelectric properties of boron rich boron carbides

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Abstract

Dense boron rich boron carbides were reactive sintered by hot pressing at 2050 °C using elementary boron−carbon compositions with carbon contents of 9.1, 11.1, 13.3 and 18.8 at.%. The following material characteristics are presented: relative density, SEM images, EDX, X-ray diffraction and corresponding lattice parameters, Seebeck coefficient, electrical conductivity and thermoelectric power factor. Significant grain growth has been obtained with increasing boron content. A deeper understanding of the boron and carbon reaction and the overall sintering process is gained by thermal and chemical analysis in combination with X-ray diffraction. Additionally a thermal experiment with boron and carbon layers illustrates the solid state diffusion behaviour. The found results of boron carbide properties of this paper correspond with results by other authors. The aim is to correlate technological aspects of sintering procedure with material properties. This should help to improve the thermoelectric efficiency of boron carbide based materials.
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1. Introduction

The use of thermoelectric materials for direct conversion of thermal energy into electrical energy is physically linked with a low efficiency. Additionally critical availability and high costs of conventional thermoelectric semiconductors (tellurides) interfere with an economic use of thermoelectric converters. Boron carbide is known as a high temperature resistant thermoelectric material.[1–3] Werheit et al.[3] did show a *ZT* of about 0.25 at 1200 K and a thermal stability up to 2000 K. The *ZT* of boron carbide is expected to increase more from 1200 K up to 2000 K.[3] Theoretically, a high efficiency of the energy conversion can be anticipated for boron carbide at temperatures >1200 K (Eq. (1)). The availability of boron carbides is much better than that of established thermoelectric materials such as tellurides or antimonites. But the low thermoelectric performance for temperatures <1200 K requires some effort in material development

before boron carbide becomes a promising candidate for thermoelectrics. A better understanding of the reactive sintering process of commercially available boron and carbon powders can help to raise the thermoelectric properties to a higher level and save cost for material manufacture.

The efficiency of the energy conversion is related to the thermoelectric degree of efficiency known as the thermoelectric figure of merit $ZT = S^2\sigma T/\kappa$ and the Carnot efficiency $\eta_C = (T_h - T_c)/T_h$. The theoretical efficiency η can be calculated according to[4]:

$$\eta = \eta_C \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h} \tag{1}$$

with the thermoelectric properties: Seebeck coefficient S, electrical conductivity σ, thermal conductivity κ, hot side temperature T_h, cold side temperature T_c and mean temperature T. The power factor $S^2\sigma$ is alternatively used to describe the thermoelectric quality of a material.

While Wood and Emin[1] and Aselage et al.[2] suggest polaron hopping as the predominant conduction mechanism in the boron carbides, Werheit[5,6] describes the electronic transport in the boron carbides as a superposition of band-type and hopping-type conduction. Boron carbide is a good p-type thermoelectric

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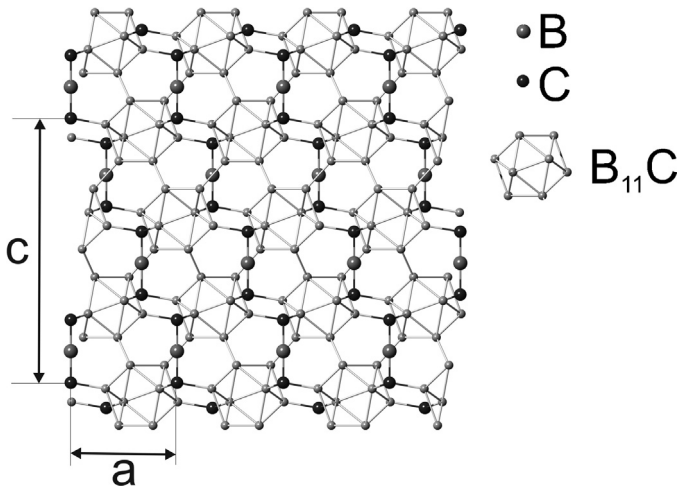 (H.-P. Martin), Alexander.Michaelis@ikts.fraunhofer.de (A. Michaelis).

Fig. 1. Section of the hypothetical B_4C structure with the lattice parameters a and c (CBC chains displayed magnified).

Table 1
Raw material characteristics.

	Amorphous boron	Graphite
Product name	Amorphous Boron Grade 1	Graphit-Pulver Feinst 4
Manufacturer	H.C. Starck, Goslar, Germany	Fuchs Lubritech GmbH, Dohna, Germany
Powder purity[a] (Minimum)	95 wt.%	99.5 wt.%
H_2O soluble[a]	0.2 wt.%	–
H_2O_2 insoluble[a]	1.0 wt.%	–
Moisture[a]	0.5 wt.%	–
O[a]	2.2 wt.%	–
N[a]	0.4 wt.%	–
Mg[a]	0.8 wt.%	–
d_{10}	0.5 μm	1.8 μm
d_{50}	1.5 μm	5.2 μm
d_{90}	4.6 μm	11.2 μm

[a] Originated from data sheet of manufacturer.

material at high temperature. Thermoelectric applications generally need well matching p- and n-type legs. One long standing problem for boron carbide was the lack of a good n-type counterpart. During the last decades, various inventive attempts have been made to obtain a matching n-type boron cluster counterpart.[7] Potential state of the art n-type candidates are homologous rare earth boron carbonitrides[8,9] and yttrium aluminium borides.[10]

Boron carbide exhibits a wide homogeneity range from 8.8 to 18.8 at.% carbon content.[11] The hypothetical B_4C structure (Fig. 1) consists of only $B_{11}C$ icosahedra and C–B–C chains. According to Werheit, the boron carbide structure has no explicit unit cell.[5] The structure consists of a certain mixture of B_{12} and $B_{11}C$ icosahedra and C–B–C, C–B–B and C–vacancy–C chains in dependence of the carbon content.[5] According to the bipolaron model favoured by Aselage and Emin, boron carbides are icosahedral borides that exist as a single phase.[2] Here, boron atoms primarily replace carbon atoms within chains, C–B–C to C–B–B with increasing boron content from $B_{4.3}C$ to $B_{13}C_2$.[2] Further increase of boron content replaces the carbon in the chains C–B–B to B–B–B from $B_{13}C_2$ to $B_{10.5}C$.[2] The bipolaron density peaks at $B_{13}C_2$.[2]

2. Materials and methods

Commercially available amorphous boron and graphite powder were used to produce boron carbide (Table 1).

2.1. Compositions and sintering parameters

Four compositions of amorphous boron and graphite (Table 2) were prepared by ball milling (PM4000, Retsch, Germany) using liquid phase sintered silicon carbide balls, isopropanol and about 0.1 wt.% of an organic dispersant (KV 5151, Zschimmer & Schwarz GmbH & Co KG, Germany).

The mass of the abrasion of the silicon carbide balls reaches about 0.7 wt.% of the starting powder mass. Hence, the abrasion of the silicon carbide balls caused an additional contamination

of the compositions with silicon, carbon and small amounts of aluminium (sintering aid of the silicon carbide balls). Every further specimen was sintered from one of these four compositions. The carbon content of initial weight c_C (Table 2) is calculated according to:

$$c_C = \frac{m_{Graphite} \cdot P_{Graphite}/M_{Carbon}}{(m_{Graphite} \cdot P_{Graphite}/M_{Carbon}) + (m_{A.Boron} \cdot P_{A.Boron}/M_{Boron})} \quad (2)$$

Each corresponding powder masse m is multiplied by the powder purity P (Table 1) and divided by the molar mass M. Hence, the carbon content of initial weight relates only to the sum of carbon and boron atoms. The powder impurities and the abrasion of the silicon carbide balls from milling are neglected for this consideration.

The carbon content of the prepared compositions was chosen according to the homogeneity range of the boron carbide phase (8.8–18.8 at.% carbon[11]). 9.1 at.% carbon were chosen instead of 8.8 at.% carbon to avoid residual boron in the sintered compacts with high certainty. Thermal analysis was done with excess carbon (20 at.%).

The Sintering parameters are shown in Table 3. The graphite die was coated by a thin film of boron nitride to impede carbon and boron diffusion between sintering compact and die.

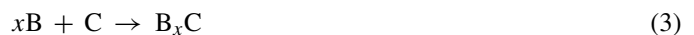During the sintering process boron and carbon react exothermically to boron carbide:

$$x B + C \rightarrow B_x C \quad (3)$$

Table 2
Amorphous boron–graphite – compositions and their carbon content of the initial weight.

Composition number	Carbon content of the initial weight (at.%)	Stoichiometry
1	9.1	$B_{10}C$
2	11.1	B_8C
3	13.3	$B_{13}C_2$
4	18.8	$B_{4.3}C$
Thermal analysis	20.0	B_4C