

# Improving the High Temperature Thermoelectric Properties of Boron Cluster Compounds through Microstructure Control

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## ABSTRACT

Novel rare earth boron icosahedral compounds have been investigated as potential high temperature thermoelectric materials. A homologous series of RE-B-C(N) boron-icosahedra-containing compounds were found to display both p-type and n-type behavior as the number of boron icosahedral layers separating the metallic layers was varied. Control of the microstructure was utilized in a new attempt to increase the figure of merit of these compounds. Hot press conditions were varied in detail and we find that the change in microstructure improves the high temperature properties. Substantial increase of the power factor  $P = \alpha^2 \sigma$  up to a factor of 3 at  $T = 1000$  K could be achieved.

**Keywords:** borides, boron carbide, thermoelectric, icosahedra, high temperature, hot press, microstructure

## 1 Introduction

In recent years the search for new thermoelectric materials is being carried out with great intensity because of the huge possibilities for useful energy conversion of waste heat for example, and the needs of modern society where the limits of classical energy resources are rapidly approaching [1]. Boron-rich cluster compounds are attractive as materials because of their stability under high temperature and acidic conditions. The magnetic properties of some recently discovered rare earth  $B_{12}$  icosahedral cluster-containing compounds have attracted increasing interest. They are magnetically dilute semiconducting/insulating materials but display a wide range of properties such as dimer-like magnetic behavior in REB<sub>50</sub>-type compounds [2], [3] or 2D spin glass behavior in a layered series of RE-B-C(N) compounds [4]–[6]. Interestingly, it has been indicated that the  $B_{12}$  icosahedral clusters play an important role in mediating the magnetic interaction which is an interesting phenomenon. Previously, boron-rich compounds such as boron carbide and doped  $\beta$ -boron systems have been investigated as possible thermoelectric materials [7], [8].

We are interested in the high temperature thermoelectric properties of  $B_{12}$  icosahedral-containing rare earth boride compounds because of their high melting points which typically exceed 2200 K and because it has been

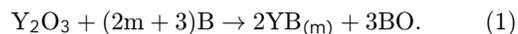
found for the REB<sub>66</sub> compound for example, that they exhibit low thermal conductivity [9], [10]. The magnitude of the thermal conductivity of REB<sub>66</sub> is one order lower than the  $\beta$ -boron compounds [9], [10]. We have previously grown crystals and investigated the high temperature thermoelectric properties of REB<sub>50</sub>-type samples [11]. REB<sub>44</sub>Si<sub>2</sub> were found to exhibit Seebeck coefficients in excess of 200  $\mu$ V/K at high temperatures above 1000 K and have a low thermal conductivity (0.027 W/cm/K at room temperature) [11].

Dresselhaus et. al has previously pointed out the attractiveness of low dimensional materials for thermoelectric properties [12]. The layered series of RE-B-C(N) compounds are interesting materials due to their 2 dimensional and also frustrated nature noted above. We have recently discovered that this homologous series of compounds display both p-type and n-type behavior as the number of boron icosahedral layers separating the metallic layers varies [13].

Synthesis of the RE-B-C(N) compounds is much more difficult than compounds like REB<sub>44</sub>Si<sub>2</sub> and REB<sub>66</sub> because the RE-B-C(N) compounds will not melt and form sizable crystals. Hot press of single phase polycrystalline powder was carried out to prepare samples for transport measurements. In this work we investigate the effect of hot press conditions on the thermoelectric properties of YB<sub>28.5</sub>C<sub>4</sub>.

## 2 Experimental

The synthesis of the single phase polycrystalline powder of YB<sub>28.5</sub>C<sub>4</sub> used in this work was carried out in the following way. First of all powders of YB<sub>m</sub> (m:12-16) were synthesized by the borothermal reduction of rare earth oxide under vacuum:



Then the desired amounts of boron and carbon were added and fired again at a reaction temperature of around 1600 °C. It is difficult to synthesize the RE-B-C(N) compounds without impurity phases such as REB<sub>6</sub> and REB<sub>12</sub> so we were very careful in controlling the composition, and multiple sintering was done in order to obtain single phase samples. The obtained single phase polycrystalline powder was treated to form samples for

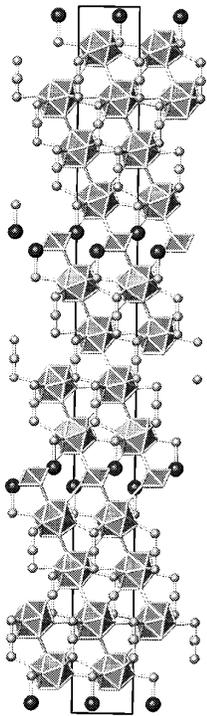


Figure 1: A view of the crystal structure of  $\text{REB}_{28.5}\text{C}_4$  perpendicular to the  $c$ -axis. The large polyhedra are  $\text{B}_{12}$  icosahedra while smaller polyhedra indicate  $\text{B}_6$  octahedra. The three bonded atoms along  $[0\ 0\ 1]$  are C-B-C chains, and the large dark circles indicate rare earth atoms.

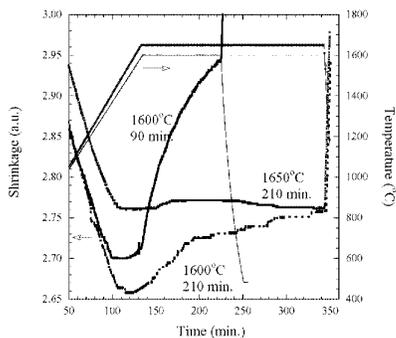


Figure 2: Time evolution of the compaction of single phase powder by the hot press method for  $\text{YB}_{28.5}\text{C}_4$ . Hot press at  $1600\text{ }^\circ\text{C}$  for 90 minutes (line),  $1600\text{ }^\circ\text{C}$  for 210 minutes (dotted line), and  $1650\text{ }^\circ\text{C}$  for 210 minutes (crosses). The temperature variation for each hot press run is also plotted versus time in corresponding thin lines.

transport measurements and this will be described in detail later. The samples were characterized by using a high resolution powder x-ray diffractometer (Rigaku Co.; RINT2000) with  $\text{Cu K}\alpha$  radiation. The structure of  $\text{YB}_{28.5}\text{C}_4$  is depicted in Fig. 1.  $\text{YB}_{28.5}\text{C}_4$  is rhombohedral (space group  $R\text{-}3\text{m}$ ) and has a layer-like structure along the  $c$ -axis, where rare earth and  $\text{B}_6$  octahedral layers are separated by four  $\text{B}_{12}$  icosahedral and C-B-C chain layers. In the limit of the number of boron icosahedral layers which separate the rare earth layers going to infinity, the compound is analogous to boron carbide.

Resistivity was measured using the four probe method. The thermoelectric power was measured by a differential method. Temperature range of the measurements was from 300 K to 1000 K. For measurements, K-type thermocouples were used instead of typical R-type thermocouples [14] because of the reactivity of platinum with boron in the upper end of this temperature range.

### 3 Results and Discussion

#### 3.1 Hot press

A hot press method at 30 MPa of the single phase polycrystalline powder packed in BN lined graphite dies was carried out. The single phase of the samples was not affected by our hot press. Various conditions of the hot press were scanned. The details of the samples are listed in Table I. Unfortunately, the hot press method by itself does not yield high density samples of the RE-B-C(N) system and all the samples were in the region of 50 % of theoretical density. There was restriction in the maximum temperature we could apply, in order to prevent impurities like  $\text{REB}_6$  from appearing, since these systems will not melt stably. Furthermore, it was not possible to directly synthesize single phase samples from the one shot hot pressing of raw materials, although various conditions were scanned. We have recently found that spark plasma synthesis and extremely high pressures of 6 GPa could yield denser samples [15]. In this work the effects of the hot press conditions on the microstructure and the thermoelectric properties are reported.

Table I: Sample details

a $\text{\AA}$	c $\text{\AA}$	conditions	d $\text{g/cm}^3$	%d <sub>th.</sub>
5.652	56.887	1600 $^\circ$ 90 m.	1.47	51.6
5.642	56.874	1600 $^\circ$ 210 m.	1.38	48.7
5.624	56.852	1650 $^\circ$ 210 m.	1.44	50.7

Time evolution of the compaction, i.e. shrinkage, of the sample by the hot press method for  $\text{YB}_{28.5}\text{C}_4$  is given in Fig. 2. The shrinkage was measured by an optical method. Hot press at  $1600\text{ }^\circ\text{C}$  for 90 minutes,  $1600\text{ }^\circ\text{C}$  for 210 minutes, and  $1650\text{ }^\circ\text{C}$  for 210 minutes. The same batch of  $\text{YB}_{28.5}\text{C}_4$  single phase polycrystalline powder was used for all 3 preparations. We note that the curve indicates that hot pressing at  $1600\text{ }^\circ\text{C}$  for a time

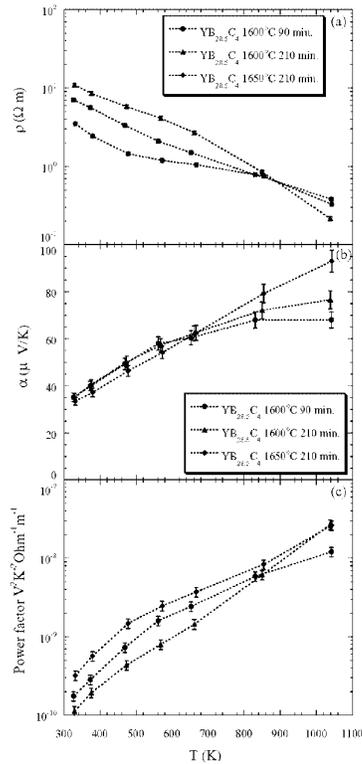


Figure 3: Temperature dependence of the (a) resistivity  $\rho$ , (b) Seebeck coefficient  $\alpha$ , and (c) power factor of  $\text{YB}_{28.5}\text{C}_4$  hot pressed at 1600°C 210 min (circles), 1600°C 90 min (triangles), and 1650°C 210 min (diamonds).

of 90 minutes appeared sufficient for sizable shrinkage with the rate decreasing quickly within the 90 minute time frame. From the densities shown in Table I we can see that increasing the hot press time from 90 minutes to 210 minutes did not yield a more densely compacted sample. In fact, for the 210 minute sample the shrinkage appears to be less smooth even under 90 minutes. Since the powder is the same batch, we can only conjecture that this difference occurred because the amount of sample pressed was larger for the 90 minute pressed sample and this had a beneficial effect. Hot pressing at 1650 °C also did not yield sizably more dense samples. And interestingly, after around 100 minutes of hot pressing the sample actually starts to expand again. Variations were observed for the thermoelectric properties at high temperatures and this will be discussed later.

### 3.2 Resistivity and thermopower

The resistivities  $\rho$  of the three differently prepared samples of  $\text{YB}_{28.5}\text{C}_4$  are plotted in Fig. 3(a). A semiconductor like dependence is observed with  $\rho$  decreasing as temperature increases. Considering a detailed

analysis of the temperature dependence, many of the boron-rich borides have been found [16] to follow the conductivity mechanism of Mott's variable range hopping mechanism for 3 dimensional systems [17] where the resistivity  $\rho$  follows:

$$\rho = \rho_0 \exp[(T_0/T)^{0.25}]. \quad (2)$$

The resistivity of our samples did not follow this dependence well. We have previously measured sintered samples of  $\text{REB}_{44}\text{Si}_2$  which similarly did not have high density but still followed the relation of Eq. 2 (albeit with very high values of characteristic temperature  $T_0$ ) [3]. This could indicate that a different conductivity mechanism is in play with these compounds. The structural similarity of our compounds to boron carbide was previously noted, with boron carbide being the infinity extrapolated limit where there are zero metal layers. In the case of the conductivity of boron carbide, the small bipolaron conduction mechanism has been proposed by Emin [7], [18]. However, the  $\sigma T$  versus  $1/T$  plot also did not show a good agreement with a linear behavior.

A possible explanation could be that there is a very large anisotropy in the conductivity mechanism of these compounds. Indeed they have anisotropic structural features where rare earth layers with close metal-metal distances are sandwiched in between boron icosahedral and C-B-C chain layers. We hope to make the conductivity mechanism of these RE-B-C(N) compounds clearer by growing crystals where it is possible to make anisotropic measurements.

The thermopower  $\alpha$ , and power factor,  $P = \alpha^2 \sigma$  are plotted in Figs. 3(b), and 3(c), respectively. Variations in the thermoelectric properties are observed to occur at the high temperatures. For the sample with highest reaction temperature and longest pressing times, we observe that the conductivity and the thermopower both increase. And despite the slightly lower densities obtained for both modified samples, the power factor values at high temperatures improve because of an increase in the Seebeck coefficient. The microstructure and/or texture of thermoelectric materials has been observed to influence the properties and it is frequently used as a strategy to improve the figure of merit [19]–[21].

The variations which we observe could be due to a modification occurring in the microstructure of sample with the more robust conditions of the hot press. Although we cannot sizably increase the hot press temperature further because of impurity formation, this result indicate that fine-tuning of the hot press conditions can be a tool for improving the qualities of this material at high temperatures. We investigate the microstructure of these samples next.

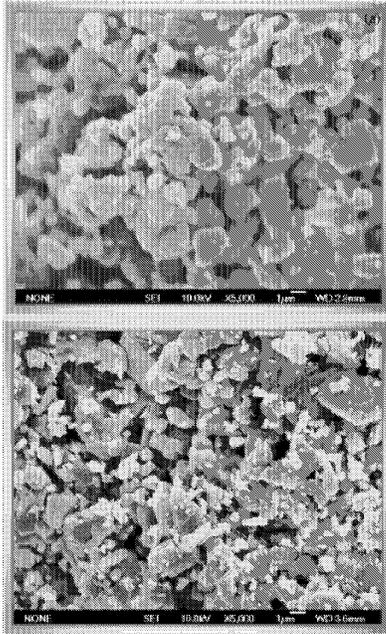


Figure 4: SEM pictures of the samples hot pressed at (a) 1600 °C for 90 minutes and (b) 1650 °C for 210 minutes.

### 3.3 Analysis of microstructure

The microstructure of the samples was investigated by a scanning electron microscope (JEOL SM-67F 10 kV). Pictures of the samples hot pressed at (a) 1600 °C for 90 minutes, and (b) 1650 °C for 210 minutes are shown in Figs. 4(a) and 4(b), respectively. Interesting differences are observed. We can see that the general size of grains are larger for sample (a), however, there appears to be a more plate-like, angular growth of the grains for sample (b). In total, the densities of the samples are similar, as noted above, and therefore we can conjecture that the plate-like, angular growth is beneficial for the high temperature properties. From the structure, this compound can be expected to have anisotropic properties. The temperature dependence of the anisotropy may be contributing more strongly in the case of sample (b).

To summarize, it is confirmed that there is indeed a change in microstructure due to the variation of hot press conditions even although the densities do not show a large difference.

### 3.4 Conclusion

We have varied the hot press conditions for a compound which is one in a potentially useful series of high temperature thermoelectric materials. These compounds have a layered structure and depending on the number of boron icosahedral layers separating the metal layers

it has been found that both p-type and n-type characteristics can be obtained. Variation in the hot press conditions yielded an increase of 3 times of the power factor at high temperatures. Although the densities do not vary largely, it is confirmed that the microstructure of the samples changes due to the difference in hot press conditions. Our results indicate that fine-tuning of the hot press conditions can be a tool for improving the thermoelectric properties of this material at high temperatures.

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