

# Thermoelectric properties of homologous p- and n-type boron-rich borides

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## Abstract

Thermoelectric properties of a series of layered homologous rare-earth boron carbonitrides:  $\text{HoB}_{17}\text{CN}$ ,  $\text{REB}_{22}\text{C}_2\text{N}$  ( $\text{RE} = \text{Y, Er, Lu}$ ), and  $\text{YB}_{28.5}\text{C}_4$ , were investigated. Samples for measurements were prepared in the form of hot pressed or isostatically pressed and annealed single phase polycrystalline powder. This series of compounds has structures where  $\text{B}_6$  octahedral and rare-earth atomic layers reside between an increasing number of  $\text{B}_{12}$  icosahedral and C–B–C chain layers, and has structural analogy to boron carbide. Interestingly, a variation from p-type thermoelectric behavior for  $\text{YB}_{28.5}\text{C}_4$  to n-type for  $\text{REB}_{22}\text{C}_2\text{N}$  and  $\text{HoB}_{17}\text{CN}$  was observed. This is the first non-doped compound among the boron-rich borides in which n-type thermoelectric behavior has been observed. Similar to other boron cluster compounds low values of the thermal conductivity  $\kappa$  ( $\kappa \leq 0.02 \text{ W cm}^{-1} \text{ K}$ ) were found. The origins of the low  $\kappa$  in such compounds has not been fully explained, but comparison among the homologous series shows that the thermal conductivity appears to increase as the number of boron cluster layers increases. This result indicates that the heavy rare-earth atoms residing in the boron matrix may play a role in depressing thermal conductivity in addition to other features common to boron cluster compounds. Although the absolute values of the determined figures of merit  $ZT$  are not large for hot pressed samples, the Seebeck coefficients and power factors for both n-type and p-type in this series show an increase at temperatures exceeding 1000 K.

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## 1. Introduction

In recent years the search for new thermoelectric materials has been carried out with great intensity, not least because of the huge possibilities for useful energy conversion of waste heat, and the needs of modern society where the limits of classical energy resources are rapidly being reached [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  $\text{B}_{12}$  icosahedral cluster-containing compounds have attracted much interest. They are magnetically dilute semiconducting/insulating materials but display a wide range of properties such as

dimer-like magnetic behavior in  $\text{REB}_{50}$ -type compounds [2,3] or 2D spin glass behavior in a layered series of  $\text{RE-B-C(N)}$  compounds [4–6]. It has been indicated that  $\text{B}_{12}$  icosahedral clusters play an important role in mediating magnetic interaction which is an interesting phenomenon. In the past, borides such as boron carbide, doped  $\beta$ -boron and  $\text{CaB}_6$  systems have been investigated as possible thermoelectric materials [7–10].

We are interested in the high-temperature thermoelectric properties of  $\text{B}_{12}$  icosahedral-containing rare-earth boride compounds because of their high melting points which are typically above 2200 K and because (this has been found for the  $\text{REB}_{66}$  compound for example), they exhibit low thermal conductivity [11,12]. The magnitude of the thermal conductivity of  $\text{REB}_{66}$  is one order lower than the  $\beta$ -boron compounds and several orders lower than the  $\text{CaB}_6$ -type compounds [11,12]. We have previously grown crystals and

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investigated the high-temperature thermoelectric properties of  $REB_{50}$ -type samples [13].  $REB_{44}Si_2$  were found to exhibit Seebeck coefficients greater than  $200 \mu V/K$  at temperatures above 1000 K and have low thermal conductivity ( $0.027 \text{ W cm}^{-1} \text{ K}$  at room temperature) [13].

Dresselhaus et al. have pointed out the attractiveness of low-dimensional materials for thermoelectric properties [14]. The layered series of  $RE-B-C(N)$  compounds are interesting materials because of their two dimensional and frustrated nature noted above. Synthesis of the  $RE-B-C(N)$  compounds is much more difficult than compounds like  $REB_{44}Si_2$  and  $REB_{66}$  because the  $RE-B-C(N)$  compounds will not melt and form sizable crystals. However, we were able to prepare samples for transport measurements and investigate their properties in this work. The homologous series of compounds of  $HoB_{17}CN$ ,  $REB_{22}C_2N$  ( $RE = Y, Er, Lu$ ), and  $YB_{28.5}C_4$ , were investigated.

## 2. Experimental

Synthesis and structure determination of these  $RE-B-C(N)$  compounds have been described previously [15]. The synthesis of the single phase polycrystalline powder of  $HoB_{17}CN$ ,  $REB_{22}C_2N$  ( $RE = Y, Er, Lu$ ), and  $YB_{28.5}C_4$  used in this work was carried out in the following way. First of all powders of  $REB_m$  ( $m: 12-16$ ,  $RE = Y, Ho, Er, Lu$ ) were synthesized by borothermal reduction of rare-earth oxide under vacuum:



Then the desired amounts of boron, carbon, and hexagonal BN, were added and fired again at a reaction temperature of around  $1600^\circ\text{C}$ . It is difficult to synthesize  $REB_{22}C_2N$  samples without impurity phases such as  $REB_6$  and  $REB_{12}$  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 compacted to form samples for 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. X-ray diffraction patterns of  $HoB_{17}CN$ ,  $YB_{22}C_2N$ , and  $YB_{28.5}C_4$  are shown in Fig. 1. Determined lattice constants are listed in Table 1. The structure of this series of compounds is depicted in Fig. 2. The compounds have layer-like structures along the  $c$ -axis, where rare earth and  $B_6$  octahedral layers are separated by  $B_{12}$  icosahedral and  $C-B-C$  chain layers of which the number increases successively from 2  $B_{12}$  layers for the  $HoB_{17}CN$  compound to 4 for the  $YB_{28.5}C_4$  compound. With respect to the limit of the number of boron icosahedral layers which separate the rare-earth layers going to infinity, the compound is like boron carbide.

Resistivity was measured using the four probe method. Thermoelectric power was measured by a differential method using a ZEM-2 apparatus manufactured by

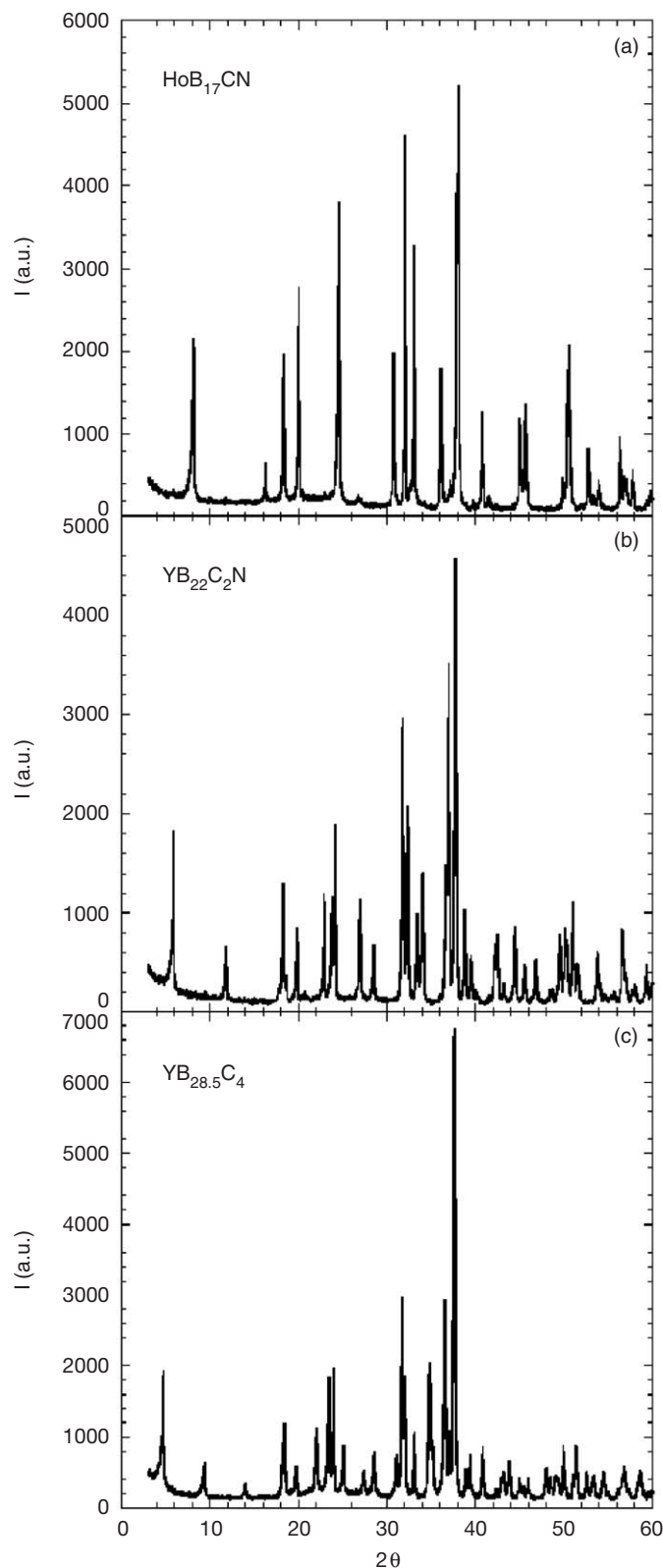


Fig. 1. X-ray diffraction patterns of (a)  $HoB_{17}CN$ , (b)  $YB_{22}C_2N$ , and (c)  $YB_{28.5}C_4$ .

ULVAC. The reliability of the apparatus has been checked by measuring a constantan standard throughout the whole temperature region. Results were reproducible.

Table 1  
Sample details

	$a$ (Å)	$c$ (Å)	Procedure	Conditions	$d$ (g/cm <sup>3</sup> )	% of theor. $d$
HoB <sub>17</sub> CN	5.586	10.827	Hot press	1600 °C 90 min	2.05	48.0
YB <sub>22</sub> C <sub>2</sub> N	5.625	44.786	RT press/anneal	1600 °C 240 min	1.58	53.3
ErB <sub>22</sub> C <sub>2</sub> N	5.630	44.704	Hot press	1600 °C 90 min	1.69	46.9
LuB <sub>22</sub> C <sub>2</sub> N	5.614	44.590	Hot press	1600 °C 90 min	1.73	47.1
YB <sub>28.5</sub> C <sub>4</sub>	5.652	56.887	Hot press	1600 °C 90 min	1.47	51.6
YB <sub>28.5</sub> C <sub>4</sub>	5.642	56.874	Hot press	1600 °C 210 min	1.38	48.7
YB <sub>28.5</sub> C <sub>4</sub>	5.624	56.852	hot press	1650 °C 210 min	1.36	47.7

Includes procedure used to compact single phase polycrystalline powder to form samples suitable for transport measurements and detailed conditions of the procedure.

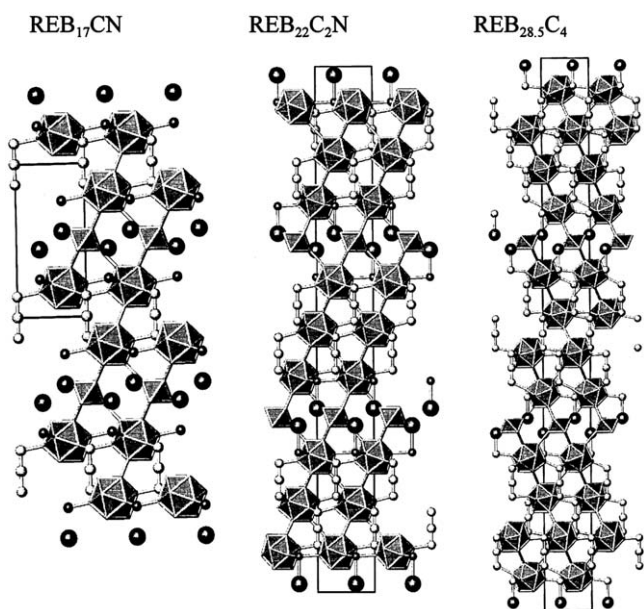


Fig. 2. A view of the crystal structures of REB<sub>17</sub>CN, REB<sub>22</sub>C<sub>2</sub>N, REB<sub>28.5</sub>C<sub>4</sub> perpendicular to the  $c$ -axis. The large polyhedra are B<sub>12</sub> icosahedra while smaller polyhedra indicate B<sub>6</sub> octahedra. The small dark circles indicate nitrogen atoms, the three bonded atoms along [001] are C–B–C chains, and the large dark circles indicate rare-earth atoms.

Temperature range of the measurements was from 300 to 1000 K. For measurements, K-type thermocouples were used instead of typical R-type thermocouples [16] because of the reactivity of platinum with boron at the upper end of this temperature range. To determine thermal conductivity, the specific heat and thermal diffusivity coefficient were measured by a laser flash method (TC-7000 ULVAC) from 300 to 1000 K.

### 3. Results and discussion

#### 3.1. Compaction of single phase polycrystalline powder samples

We used two methods to compact samples suitable for transport measurements. First, single phase polycrystalline

powder was isostatically pressed at 300 MPa and then annealed. Secondly, a hot press method at 30 MPa of the single phase polycrystalline powder packed in boron nitride-lined graphite dies was carried out. The single phase of the samples was not affected by either method of compaction. Both methods yielded similar densities of samples. In the case of YB<sub>28.5</sub>C<sub>4</sub>, various conditions of the hot press were scanned. The details of the samples are listed in Table 1. Unfortunately, we were unable to obtain high-density samples of the RE–B–C(N) system and all the samples were in the region of 50% of theoretical density. The maximum temperature we could apply was limited, in order to prevent impurities 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, since impurity phases such as REB<sub>6</sub> and REB<sub>12</sub> would appear.

Single phase polycrystalline powder of HoB<sub>17</sub>CN, REB<sub>22</sub>C<sub>2</sub>N ( $RE = Er, Lu$ ), and YB<sub>28.5</sub>C<sub>4</sub> were hot pressed under the same condition of 30 MPa and 1600 °C for 90 min under Ar gas. Time evolution of the compaction, i.e. shrinkage, of the sample by the hot press method for YB<sub>28.5</sub>C<sub>4</sub> is given in Fig. 3. The shrinkage was measured by an optical method. Three different conditions were tried in the case of YB<sub>28.5</sub>C<sub>4</sub>: hot press at 1600 °C for 90 min, 1600 °C for 210 min, and 1650 °C for 210 min. The same batch of YB<sub>28.5</sub>C<sub>4</sub> single phase polycrystalline powder was used for all three preparations. We note that the curve indicates that hot pressing at 1600 °C for a time of 90 min appeared sufficient for sizable shrinkage with the rate decreasing quickly within the 90 min time frame. From the densities shown in Table 1 we can see that increasing the hot press time from 90 to 210 min did not yield a more densely compacted sample. In fact, for the 210 min sample the shrinkage appears to be less smooth even under 90 min. 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 min pressed sample and this had a beneficial effect. Hot pressing at 1650 °C also did not yield more dense samples. And interestingly, after around 100 min of hot pressing the sample actually starts to expand again. Small variations were observed for

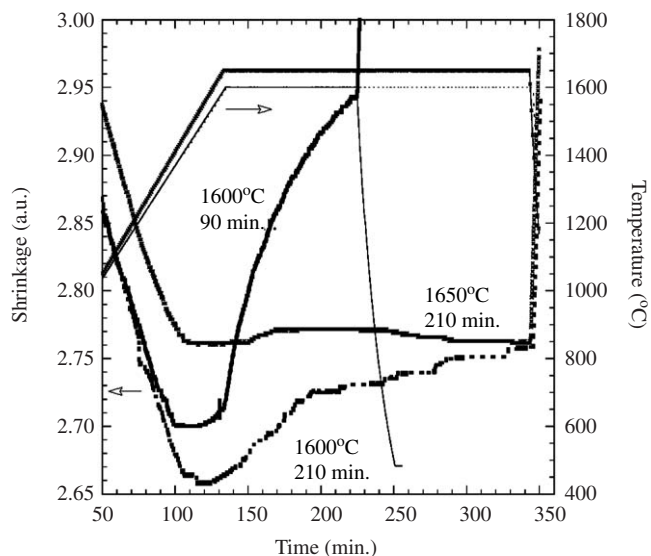


Fig. 3. Time evolution of the compaction of single phase powder by the hot press method for  $\text{YB}_{28.5}\text{C}_4$ . Hot press at  $1600^\circ\text{C}$  for 90 min (line),  $1600^\circ\text{C}$  for 210 min (dotted line), and  $1650^\circ\text{C}$  for 210 min (crosses). The temperature variation for each hot press run is also plotted versus time in corresponding thin lines.

thermoelectric properties at high temperatures and this will be discussed later.

The  $\text{YB}_{22}\text{C}_2\text{N}$  sample was prepared by isostatically pressing single phase polycrystalline powder at room temperature and then annealing for 4 h at  $1600^\circ\text{C}$  under Ar gas. As can be seen from Table 1, the density of the sample is similar to the hot pressed samples.

### 3.2. Resistivity and thermopower

The resistivity of  $\text{HoB}_{17}\text{CN}$ ,  $\text{REB}_{22}\text{C}_2\text{N}$  ( $\text{RE} = \text{Y, Er, Lu}$ ), and  $\text{YB}_{28.5}\text{C}_4$  is plotted in Figs. 4(a) and (b). Fig. 4(a) shows the logarithm of the resistivity plotted versus  $T^{-0.25}$ . Many of the boron-rich borides have been found [17,18] to follow the conductivity mechanism of Mott's variable range hopping mechanism for three-dimensional systems [19,20] where the resistivity  $\rho$  follows:

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

We note that the data of our compounds do not appear to follow a straight line in Fig. 4(a). 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 for the 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 boron carbide, two mechanisms have been proposed for conductivity. The small bipolaron conduction mechanism proposed by Emin [7,21] and conduction governed by band splitting due to the Jahn–Teller effect

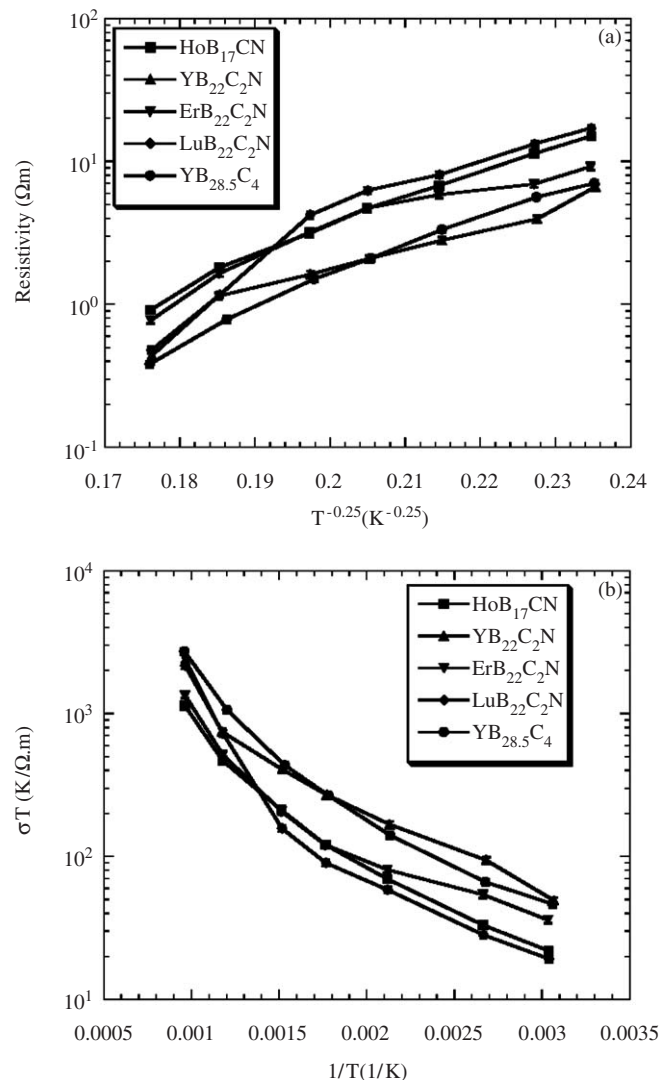


Fig. 4. Temperature dependence of resistivity of  $\text{HoB}_{17}\text{CN}$  (squares),  $\text{YB}_{22}\text{C}_2\text{N}$  (triangles),  $\text{ErB}_{22}\text{C}_2\text{N}$  (reversed triangles),  $\text{LuB}_{22}\text{C}_2\text{N}$  (diamonds), and  $\text{YB}_{28.5}\text{C}_4$  (circles) plotted as (a)  $\ln \rho$  versus  $T^{-0.25}$ , (b)  $\sigma T$  versus  $1/T$ . The lines are guides to the eye.

proposed by Werheit [22]. We try plotting our data in the  $\sigma T$  versus  $1/T$  plot in Fig. 4(b) following Ref. [7]. The agreement with a linear dependence is also not good for the data.

A possible explanation for the above results 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. The detailed conductivity mechanism of the homologous  $\text{RE–B–C(N)}$  compounds should be the topic of future investigation.

Regarding the absolute values of resistivity, it appears that  $\rho$  generally becomes higher as the number of metal layers is increased from  $\text{YB}_{28.5}\text{C}_4$  to  $\text{HoB}_{17}\text{CN}$ , going further away from boron carbide. This tendency is observed even after taking into account possible effects



from differences in density, i.e.  $\text{YB}_{22}\text{C}_2\text{N}$  which has higher density than  $\text{YB}_{28.5}\text{C}_4$  still has higher resistivity, while  $\text{HoB}_{17}\text{CN}$  has higher or similar resistivity despite having higher density than  $\text{ErB}_{22}\text{C}_2\text{N}$  and  $\text{LuB}_{22}\text{C}_2\text{N}$ .

The resistivity of all the measured  $RE\text{-B-C(N)}$  samples here are relatively high compared to boron carbide [7] or measured crystal samples of  $RE\text{B}_{44}\text{Si}_2$  [13], for example. We are presently trying to prepare dense samples close to 100% of the theoretical value by using special apparatus to perform the hot press at 6 GPa. Spark plasma synthesis (SPS) is also being carried out.

The Seebeck coefficients  $\alpha$  of  $\text{HoB}_{17}\text{CN}$ ,  $RE\text{B}_{22}\text{C}_2\text{N}$  ( $RE = \text{Y, Er, Lu}$ ), and  $\text{YB}_{28.5}\text{C}_4$  are plotted in Fig. 5. The most striking result is that we observe n-type behavior for the  $RE\text{B}_{22}\text{C}_2\text{N}$  ( $RE = \text{Y, Er, Lu}$ ) and  $\text{HoB}_{17}\text{CN}$  sample. Starting with boron carbide, the boron-rich boride compounds discovered up to now have all shown p-type behavior [7,13]. n-type behavior has been observed for  $\beta$ -boron doped with substantial amounts of transition metals [23–25], but this is the first example of n-type behavior ever observed for a non-doped boron-rich boride compound.

It is interesting to note that the compound with smallest proportion of metal layers;  $\text{YB}_{28.5}\text{C}_4$ , shows the usual p-type behavior. This indicates that the two-dimensional metal layers of these  $RE\text{-B-C(N)}$  compounds play a role in the unusual n-type behavior.

However, the dependence is not simple since  $RE\text{B}_{22}\text{C}_2\text{N}$  takes larger absolute values of  $\alpha$  compared to  $\text{HoB}_{17}\text{CN}$ . Furthermore, there is a relatively large  $RE$  dependence as is observed for the different  $RE\text{B}_{22}\text{C}_2\text{N}$  ( $RE = \text{Y, Er, Lu}$ ) samples. This indicates that the relevant band structures of these  $RE\text{-B-C(N)}$  compounds are sensitive to modifications brought on by small changes in the lattice constant from the different sizes of the rare earths. As noted for the resistivity results, investigation of the anisotropic transport

properties should make clearer the particular effect of the two-dimensional rare-earth layers. Crystals of these compounds large enough to measure have not yet been obtained, but we will continue efforts to grow them.

Regarding possible alternative sources for the n-type behavior, we can disregard variation in the oxidation states of the metals, because magnetic measurements have indicated trivalent states for all of the compounds [4–6]. However, we need to take into account possible effects of nitrogen, since the n-type  $\text{HoB}_{17}\text{CN}$  and  $RE\text{B}_{22}\text{C}_2\text{N}$  contain the electronegative nitrogen element while the p-type  $\text{YB}_{28.5}\text{C}_4$  does not. We have previously found that it is possible to synthesize  $RE\text{B}_{22}\text{C}_2\text{N}$  with carbon replacing the nitrogen atom; such samples will be prepared and measured to investigate this further in our next work.

Incidentally, one of our motivations to investigate these compounds was that they had previously been found to have magnetic frustration originating from the flat triangular configuration of the metal atoms in the basal plane [4–6]. It was discovered for  $\text{NaCo}_2\text{O}_4$  that an anomalously large Seebeck effect exists [26]. The thermopower was found to be 10 times larger than expected for a typical metal.  $\text{NaCo}_2\text{O}_4$  has a two-dimensional triangular lattice of Co atoms and the authors speculated that this large thermopower may possibly originate from spin fluctuation although it has not been explicitly proved yet. From comparison in Fig. 5 of the thermopower of magnetic  $\text{ErB}_{22}\text{C}_2\text{N}$  to that of the non-magnetic  $\text{YB}_{22}\text{C}_2\text{N}$  and  $\text{LuB}_{22}\text{C}_2\text{N}$ , we observe that there does not appear to be any enhancement of the  $|\alpha|$  from the magnetic frustration known to exist [4–6] in this  $RE\text{-B-C(N)}$  system.

Finally, the absolute values of the thermopower are not as big as those of boron carbide [7] or  $RE\text{B}_{44}\text{Si}_2$  [13] but they appear to generally increase with temperature up to 1000 K and beyond.

The power factors of thermoelectric materials are given as

$$P = \alpha^2 / \rho. \quad (3)$$

Values of  $P$  for the measured samples here are not large, being less than  $10^{-8} \text{ V}^2 \text{ K}^{-2} \Omega^{-1} \text{ m}^{-1}$ . This is due in large part to poor conductivity and we hope to improve this with denser samples and more so by doping as will be discussed in the next section. As expected from Figs. 4 and 5, the power factor for all the homologous  $RE\text{-B-C(N)}$  samples increases with temperature up to and above 1000 K.

### 3.3. Thermal conductivity

To evaluate the attractiveness of compounds as thermoelectric materials, it is necessary to determine the dimensionless figure of merit  $ZT = PT/\kappa$ , where  $\kappa$  is the thermal conductivity. We determined the thermal conductivity of the homologous series of compounds;  $\text{HoB}_{17}\text{CN}$ ,  $\text{ErB}_{22}\text{C}_2\text{N}$ , and  $\text{YB}_{28.5}\text{C}_4$ , by measuring the specific heat

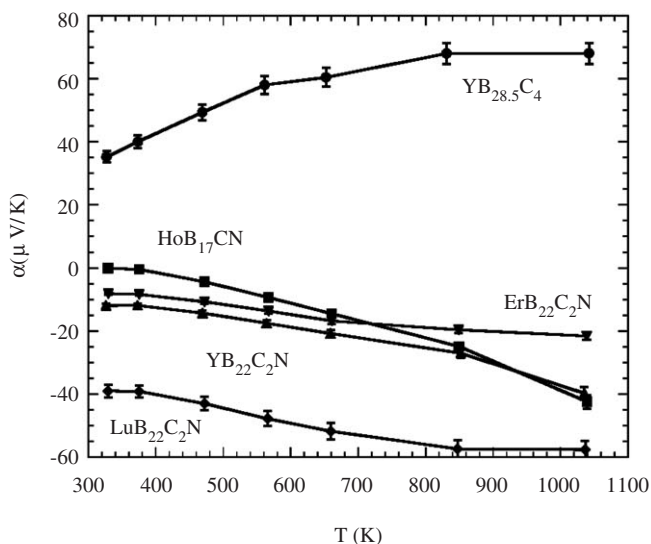


Fig. 5. Temperature dependence of the Seebeck coefficient  $\alpha$  of  $\text{HoB}_{17}\text{CN}$  (squares),  $\text{YB}_{22}\text{C}_2\text{N}$  (triangles),  $\text{ErB}_{22}\text{C}_2\text{N}$  (reversed triangles),  $\text{LuB}_{22}\text{C}_2\text{N}$  (diamonds), and  $\text{YB}_{28.5}\text{C}_4$  (circles). The lines are guides to the eye.

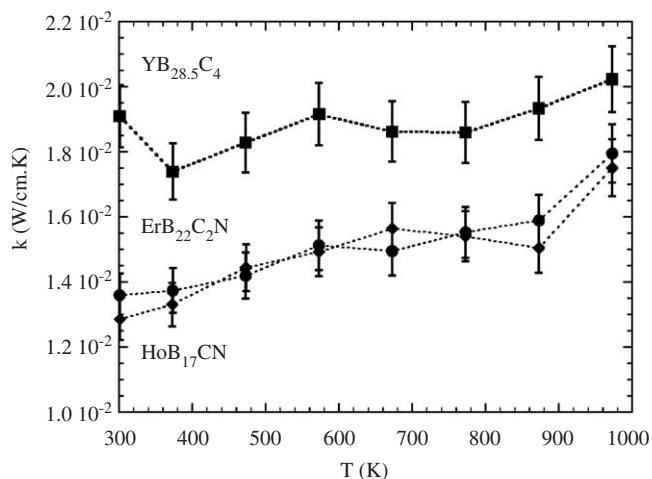


Fig. 6. Temperature dependence of the thermal conductivity  $\kappa$  of HoB<sub>17</sub>CN (diamonds), ErB<sub>22</sub>C<sub>2</sub>N (circles), and YB<sub>28.5</sub>C<sub>4</sub> (squares). The lines are guides to the eye.

$C$  and the thermal diffusivity coefficient  $D_t$  of the samples:

$$\kappa = C \cdot D_t \cdot d, \quad (4)$$

where  $d$  is the density.  $\kappa$  is shown in Fig. 6. We observe that the thermal conductivity of these compounds is quite low, for example taking a value of  $0.013 \text{ W cm}^{-1} \text{ K}$  at room temperature in the case of HoB<sub>17</sub>CN. The relatively low density of the samples likely play a role for these extremely low values which are even smaller than other rare-earth boron cluster compounds like REB<sub>66</sub> [11,12] and REB<sub>44</sub>Si<sub>2</sub> [13]. However, since the samples measured in this work were synthesized under the same conditions with similar densities, we can make a meaningful comparison within the homologous series. And although the values for HoB<sub>17</sub>CN and ErB<sub>22</sub>C<sub>2</sub>N are close, it appears there is a dependence on the homologous series with thermal conductivity actually increasing as the number of boron cluster layers increase.

The origin of the generally low values of  $\kappa$  found in the boron icosahedral compounds is considered. First of all, the fivefold symmetry of the boron icosahedra which are the building blocks of the structure in these boron-rich compounds obviously not translating to the symmetry of the crystal structure have been suggested to play a role [11,12]. We previously noted that the rare-earth B<sub>12</sub> icosahedral cluster compounds in which rare-earth atoms occupy voids among the clusters, generally appear to have lower thermal conductivity [13] than boron cluster compounds like  $\beta$ -boron and boron carbide [27] which do not contain heavy metal atoms. The results obtained here, which are a direct comparison of a homologous series of compounds also agrees with this tendency, viz. the sample with more metallic layers appear to have a lower  $\kappa$ . It has previously been proposed for skutterudite compounds that the metal atoms in the matrix act as rattlers and reduce  $\kappa$  [28,29]. Considering the rare-earth icosahedral compounds, the equivalent isotropic thermal parameters of rare-earth

atoms in REB<sub>44</sub>Si<sub>2</sub>, for example, is indeed not small,  $B = 0.22 \text{ \AA}^2$ . However, it is not especially large compared to the boron atoms themselves. Another factor which should probably be taken into account for the boron cluster compounds is the compositional disorder. There are typically partially occupied boron sites (not in the icosahedra). And in the case of YB<sub>66</sub> the yttrium atoms have an occupancy of only about 55%. For REB<sub>44</sub>Si<sub>2</sub>, Si partially replaces B in the B<sub>15</sub> polyhedron and causes additional disorder. The RE-B-C(N) compounds also have partial occupancy of the rare-earth sites. In addition, Wood et al. have reported seeing effects of compositional disorder on thermal conductivity in a series of boron carbide samples with different carbon contents [27].

Further systematic study of the thermal conductivity of the newly discovered rare-earth boron icosahedral compounds should shed more light on the origin of low  $\kappa$  in this class of compounds and the possible role the rare-earth atoms play. Regarding the homologous RE-B-C(N) series, a systematic investigation of the effect of the different rare earths on  $\kappa$  should also yield more information.

We can estimate the figure of merit ZT for these compounds by smoothly extrapolating our measured data in the form of polynomials (Fig. 7). For this estimation we assume that the thermal conductivity values for the different rare-earth phases of REB<sub>22</sub>C<sub>2</sub>N are basically the same. The absolute values of ZT are small compared with values such as ZT~1 for bismuth telluride at room temperature [1]. However, as noted before, the densities of the samples are not high being only ~50% of the theoretical value, and with the extreme high pressure 6 GPa pressing and SPS being carried out now, high-density samples with lower resistivities are expected. Denser samples lead to higher thermal conductivities and for

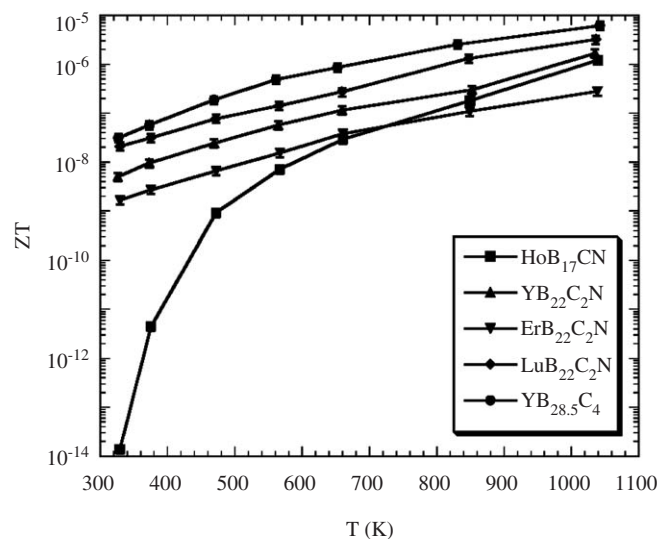


Fig. 7. Temperature dependence of the estimated figure of merit ZT of HoB<sub>17</sub>CN (squares), YB<sub>22</sub>C<sub>2</sub>N (triangles), ErB<sub>22</sub>C<sub>2</sub>N (reversed triangles), LuB<sub>22</sub>C<sub>2</sub>N (diamonds), and YB<sub>28.5</sub>C<sub>4</sub> (circles). The lines are guides to the eye.

oxides like  $\text{NaCo}_2\text{O}_4$  for example, a large improvement in ZT was not obtained even though resistivity was decreased [30]. However, our samples are fundamentally different, since very low thermal conductivity values are intrinsically expected for these boron icosahedral cluster compounds. With established results of very low  $\kappa$  for all such boron icosahedral compounds, including single crystal samples, we do not expect  $\kappa$  to increase so greatly as to be

detrimental even if samples are densified. Furthermore, the presented results are for compounds as is and we hope to improve the properties by doping, since boron cluster compounds typically have open voids which can accommodate dopant atoms. Large modifications of the thermoelectric properties have in the past successfully been obtained, e.g. for the  $\beta$ -boron system, through doping with transition metals [23–25]. Substantial improvements to the properties of boron carbide have also been successfully obtained by modifying the carbon content [7]. Work will also be done to vary the carbon and nitrogen content of these  $RE\text{-B-C(N)}$  compounds and investigate the effects on the thermoelectric properties.

As an attractive high-temperature characteristic, ZT shows an increase with increasing temperature above 1000 K. To summarize, the important result obtained here is that we have discovered an unmodified high-temperature n-type compound as a starting point for further investigations.

#### 3.4. Comparison of $\text{YB}_{28.5}\text{C}_4$ compounds prepared under different conditions

We tried three modifications of the hot press conditions for  $\text{YB}_{28.5}\text{C}_4$  as noted above.  $\rho$ , thermopower, and power factor are plotted in Figs. 8(a)–(c), respectively. Variations in the thermoelectric properties are observed at high temperatures. For the sample with highest reaction temperature and longest pressing times, we observe that conductivity and thermopower both increase. And despite the slightly lower densities obtained for both modified samples, the ZT values at high temperatures improve because of an increase in the Seebeck coefficient. The microstructure and/or texture of thermoelectric materials has been found to influence the properties and it is frequently used as a strategy to improve the figure of merit [31–33].

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, our results indicate that fine tuning of the hot press conditions can be a tool for improving the qualities of this material at high temperatures. Detailed analysis of the microstructure of our samples by TEM for example, will also be carried out next to make the behavior clearer.

#### 4. Conclusions

We have synthesized single phase polycrystalline powder of the homologous  $RE\text{-B-C(N)}$  compounds which have a structural analogy to boron carbide, and mainly utilized the hot press method to compact samples suitable for transport measurement to investigate thermoelectric properties. The  $RE\text{-B-C(N)}$  compounds have pairs of flat two-dimensional triangular layers of rare-earth metals incorporating  $\text{B}_6$  octahedra separated by  $\text{B}_{12}$  icosahedral and

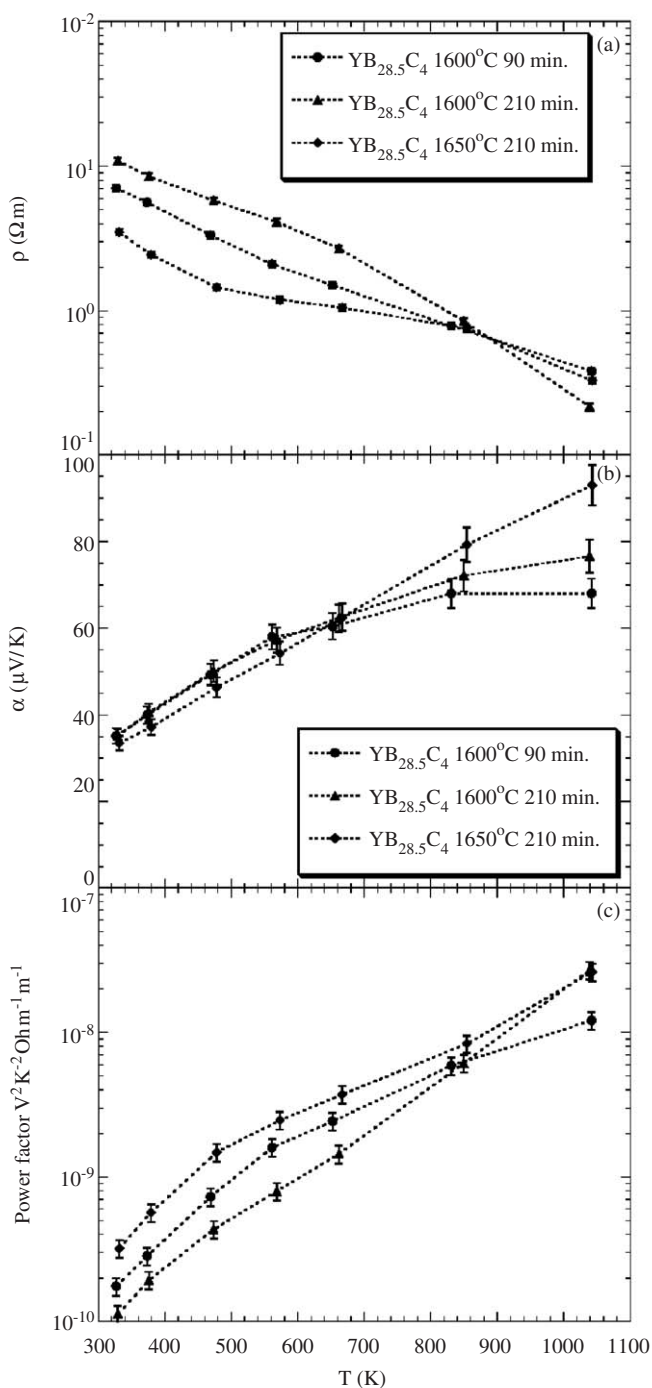


Fig. 8. Temperature dependence of the (a) resistivity  $\rho$ , (b) Seebeck coefficient  $\alpha$ , and (c) power factor of  $\text{YB}_{28.5}\text{C}_4$  hot pressed at 1600°C 210 min (circles), 1600°C 90 min (triangles), and 1650°C 210 min (diamonds). The lines are guides to the eye.

C–B–C chain layers. The hot press method at 30 MPa only yielded samples with densities around 50% of theoretical density. Accordingly, values of conductivity were poor, but important information was gained as to thermoelectric properties. N-type behavior was discovered for the  $REB_{22}C_2N$  ( $RE = Y, Er, Lu$ ) and  $HoB_{17}CN$  samples. These are the first examples of unmodified boron-rich boride compounds exhibiting n-type behavior. The  $YB_{28.5}C_4$  compound with the least number of rare-earth layers was found to exhibit the typical p-type behavior.

The thermal conductivity of the homologous series was also measured and low values  $\kappa \leq 0.02 \text{ W cm}^{-1} \text{ K}$  were observed for all the compounds for  $300 \text{ K} \leq T \leq 1000 \text{ K}$ . Although the low density of the samples may be playing a role contributing to the low absolute values of  $\kappa$ , a comparison indicated that with increasing number of boron cluster layers, thermal conductivity actually increases. This indicates that the heavy rare-earth atoms in the light boron matrix may be playing an active role in lowering thermal conductivity.

Different conditions for the hot press compaction yielded improvements in the thermoelectric characteristics at high temperature possibly originating from differences in the microstructure and this will be further pursued. Work is underway to prepare high-density samples at 6 GPa and also to utilize spark plasma synthesis (SPS). We stress again that the most important result obtained is that we have discovered an unmodified high-temperature n-type compound as a starting point for further investigations.

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