Origin of the n-type behavior in rare earth borocarbide $Y_{1-x}B_{28.5}C_4$

Takao Mori,[*a,b,c] **Toshiyuki Nishimura,**[a] **Walter Schnelle,**[d] **Ulrich Burkhardt**[d] **and Yuri Grin**[d]

Synthesis conditions, morphology, and thermoelectric properties of $Y_{1-x}B_{28.5}C_4$ were investigated. $Y_{1-x}B_{28.5}C_4$ is the compound with the lowest metal content in a series of homologous rare earth borocarbonitrides, which have been attracting interest as high temperature thermoelectric materials because they can embody the long awaited counterpart to boron carbide, one of the few thermoelectric materials with a history of commercialization. It was revealed that the presence of boron carbide inclusions was the origin of the p-type behavior 10 previously observed for $Y_{1-x}B_{28.5}C_4$ in contrast to $Y_{1-x}B_{15.5}CN$ and $Y_{1-x}B_{22}C_2N$. In comparison to that of previous small flux-grown single crystals, a metal-poor composition of $YB_{40}C_6$ ($Y_{0.71}B_{28.5}C_4$) in the synthesis successfully yielded sintered bulk $Y_{1-x}B_{28.5}C_4$ samples apparently free of boron carbide inclusions. "Pure" $Y_{1-x}B_{28.5}C_4$ was found to exhibit the same attractive n-type behavior similar to the other rare earth borocarbonitrides even though it is the most metal-poor compound among the rare earth borocarbonitride series. Calculations of the electronic structure were carried out for $Y_{1-x}B_{28.5}C_4$ as a representative of the series of homologous compounds and 15 reveal a pseudo gap-like electronic density of states near the Fermi level mainly originating from the covalent borocarbonitride network.

Introduction

Development of thermoelectric materials is being vigorously carried out throughout the world now, in an effort to find new 20 ways to save energy [1]. One need exists to develop mid to high temperature thermoelectric materials for waste heat power generation in thermal power plants, steelworks, incinerators, and utilizing focused solar power, etc. The performance of thermoelectric materials can be gauged by the figure of merit *ZT* 25 $= S^2T/\rho\kappa$, where S, ρ, κ and T are the Seebeck coefficient, electrical resistivity, thermal conductivity and absolute temperature, respectively.

Boron cluster compounds are attractive candidates as high temperature thermoelectric materials for their stability and 30 generally large Seebeck coefficients [2-4]. Furthermore, they have been found to typically possess low thermal conductivity [5-8], an inherent advantage for thermoelectric application, despite being strongly covalently bonded solids with high sound velocity.

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55 Several mechanisms have been proposed to be the origin of this phenomenon [4,8,9]. Another attractive feature is that the network structures and physical properties of boron cluster compounds have been found to be able to be controlled to some degree through incorporation of rare earth or other metal atoms in 60 the voids of clusters, and also addition of third elements like C, N, Si which can act as bridging sites within the framework[10,11].

Up to now, the thermoelectric properties of boron cluster compounds such as boron carbide [2,12-17], β-boron based 65 materials [18-22], B_6S_{1-x} [23], RB_{66} [24,25] (R = rare earth), $RB_{44}Si_2$ [3,8,26,27], $MgAlB_{14}$ [28], $Y_xAl_yB_{14}$ [29-31], have been investigated in detail.

Boron carbide is especially notable because it is one of the few thermoelectric materials with a history of commercialization. 70 However, a critical problem with boron carbide was a lack of similar material with n-type, since effective thermoelectric modules require well matching p- and n-type legs. As a possible solution to this long standing problem, a series of rare earth

Figure 1: View of the crystal 40 structure of the homologous rare earth borocarbonitride series and boron carbide "B₄C". The large and small polyhedra indicate B_{12} icosahedra and B_6 octahedra, respectively. The small 45 circles indicate nitrogen atoms, the three bonded atoms perpendicular to the [0 0 1] direction are C-B-C chains with open circles indicating carbon atoms, and the large circles are rare 50 earth atoms.

$R_{1-x}B_{15.5}CN$ $R_{1-x}B_{22}C_2N$ $R_{1-x}B_{28.5}C_4$ "B₄C"
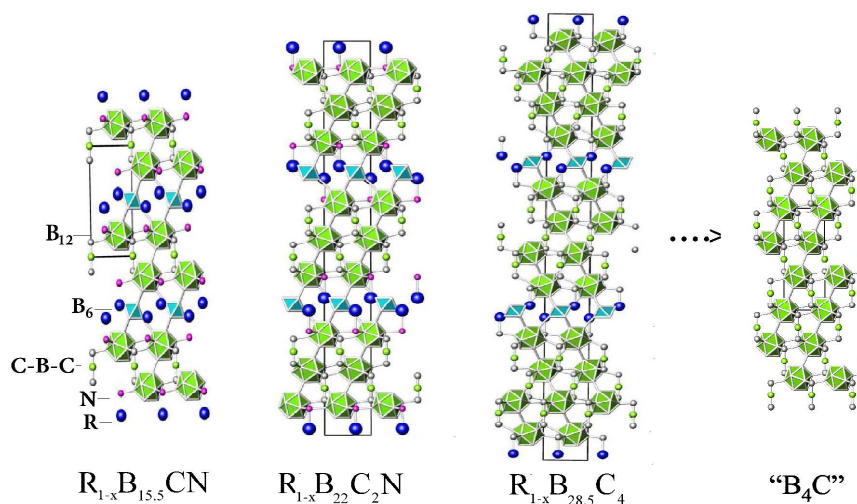
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borocarbonitrides $R_{1-x}B_{15.5}CN$, $R_{1-x}B_{22}C_2N$, and $R_{1-x}B_{28.5}C_4$ compounds was synthesized. While $R_{1-x}B_{15.5}CN$ and $R_{1-x}B_{22}C_2N$ were discovered to exhibit intrinsic n-type behavior, $R_{1-x}B_{28.5}C_4$ was reported to have p-type behavior [32-36]. This series of compounds have crystal structures which are homologous to boron carbide (Fig. 1), therefore they can be good matching n-type counterparts to p-type boron carbide. It was initially thought that $R_{1-x}B_{28.5}C_4$ was p-type, which was thought reasonable on the surface since it is the most boron-rich (metal-poor) compound and furthermore does not contain the electronegative element N. Rather the n-type behavior of $R_{1-x}B_{15.5}CN$ and $R_{1-x}B_{22}C_2N$ was striking, since such intrinsic behavior was observed for the first time in compounds containing boron icosahedra in the crystal structure. In the present work, the true nature of electronic transport behavior of $R_{1-x}B_{28.5}C_4$ is revealed.

Experimental

As described previously [32], synthesis of the homologous rare earth borocarbonitrides, $R_{1-x}B_{15.5}CN$, $R_{1-x}B_{22}C_2N$, and $R_{1-x}B_{28.5}C_4$, is typically carried out in the following way. Powders of RB_n are prepared with the borothermal reduction method at 2000 K in BN crucibles with graphite susceptors:

$$R_2O_3 + (2n+3)B \rightarrow 2RB_n + 3BO$$
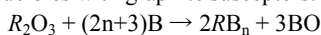
Then the desired amounts of boron and carbon are added and fired again at a reaction temperature of around 1900 K. It was usually difficult to synthesize rare earth borocarbonitride samples without impurity phases such as RB_6 and RB_{12}, and multiple sintering was typically done in order to obtain single phase samples. The samples with the starting composition $Y_{0.83}B_{28.5}C_4$ were prepared in the same way for this work. However, as shown later, it was revealed that boron carbide inclusions exist in the finally prepared samples. We label these samples as "conventional" $Y_{1-x}B_{28.5}C_4$. The obtained polycrystalline "conventional" $Y_{1-x}B_{28.5}C_4$ was hot pressed to form specimens for the measurements.

With the following method we were successful in synthesizing $Y_{1-x}B_{28.5}C_4$ free of boron carbide inclusions. The yttrium site in $Y_{1-x}B_{28.5}C_4$ was previously determined to have a partial occupancy of 83% ($Y_{0.83}B_{28.5}C_4$) from single crystal XRD analysis on small crystals grown by the flux method [37]. Therefore, the actual chemical composition of single crystal samples can be written as $YB_{34.3}C_{4.8}$. From extensive trial and error and tuning of the synthesis conditions, it was finally discovered that starting from a metal-poor composition compared to that of the flux grown single crystal, of $YB_{40}C_6$ was the successful condition to obtain sintered samples apparently free of the boron carbide. The starting composition is counterintuitive on the surface, since from normal expectations, it would seem advantageous to use a metal-rich mixture in order to inhibit boron carbide formation. However, the success of the apparently metal-poor mixture may be due to differences in metal occupancy between flux grown crystals and sintered samples as was observed for aluminoborides [29]. In any case "pure" $Y_{1-x}B_{28.5}C_4$ was finally obtained. To write in detail the full synthesis process, YB_n obtained by the borothermal method as described above together with B and C used as starting materials and a mixture of

$YB_{40}C_6$ was isostatically cold pressed at 300 MPa. These pellets were then sintered at ~1600°C for 10 hours under argon.

As described before [32,33], densities of "conventional" $Y_{1-x}B_{28.5}C_4$ or rare earth borocarbonitride samples cold pressed at 300 MPa and then sintered, or hot pressed, only reached values around half the theoretical density. Incidentally with SPS it was previously found that the densities could be increased to ~75% with spark plasma sintering (SPS) [33] or further to even 95% with additives in SPS [35,38]. For simply cold pressed "pure" $Y_{1-x}B_{28.5}C_4$ the achieved density was a little higher than the "conventional" case and reached ~65%.

Resistivity and thermoelectric power were measured at high temperatures of 300 to 1050 K using an ULVAC ZEM-2, while the high temperature thermal diffusivity coefficient and specific heat were measured by using an ULVAC TC-7000 to obtain the thermal conductivity. The thermoelectric properties below 300 K were measured by using the TTO option of the PPMS (Quantum Design).

Samples were characterized by powder x-ray diffraction and observation of morphology was done with a scanning electron microscope SEM (JEOL SM-67F 10 kV).

The band structure and electronic density of states were calculated for the ordered model with the composition $Y_1B_{29.5}C_4$ [39] using the density functional theory (DFT) within a local-density approximation (LDA) with the Barth-Hedin's exchange potential [40]. The yttrium compound was especially suitable allowing to avoid known difficulties in description of the f states by LDA. The atomic coordinates and lattice parameters were taken from Ref. 37. The defect occupation of the yttrium position was taken in account within the rigid-band approximation.

Within the program package TB-LMTO-ASA [41] the radial scalar-relativistic Dirac equation was solved to get the partial waves. The following radii of the atomic spheres were applied for the calculations: $r(Y) = 1.948$ Å, $r(B1) = 1.016$ Å, $r(B2) = 1.026$ Å, $r(B3) = 1.221$ Å, $r(B4) = 1.213$ Å, $r(B5) = 1.200$ Å, $r(B6) = 1.213$ Å, $r(B7) = 1.221$ Å, $r(B8) = 1.206$ Å, $r(B9) = 1.178$ Å, $r(B10) = 1.227$ Å, $r(B11) = 1.204$ Å, $r(B12) = 1.181$ Å, $r(C1) = 1.005$ Å, $r(C2) = 1.022$ Å, $r(C3) = 0.998$ Å, $r(C4) = 1.008$ Å. Because the calculation within the atomic sphere approximation (ASA) includes corrections for the neglect of interstitial regions and partial waves of higher order [42], an addition of empty spheres was necessary because of the strongly pronounced cage character of the crystal structure: $r(E1) = 1.334$ Å, $r(E2) = 1.354$ Å, $r(E3) = 1.268$ Å. Basis sets containing $Y(5s,4d)$, $B(2s,2p)$, and $C(2s,2p)$ orbitals was employed for a self-consistent calculation with $Y(5p,4f)$, $B(3d)$, and $C(3d)$ functions being downfolded.

Results and Discussion

An investigation of the microstructure of "conventional" $Y_{1-x}B_{28.5}C_4$ samples by SEM revealed the existence of some secondary phase in the form of grains with whitish contrast as shown in Fig. 2(a).

A closer examination of the XRD of this compound with high resolution experiments showed that small amounts of boron carbide (Fig. 3 top pattern, arrows) and possibly even smaller amounts of another representative of the yttrium borocarbonitride homologous series were present in the sample. Due to the obviously similar structure fragments in

boron carbide, $Y_{1-x}B_{28.5}C_4$ and other yttrium borocarbonitrides (Fig. 1) there are overlaps of the diffraction reflections in the XRD pattern and it was previously overlooked. Previous chemical analysis also did not reveal the presence of the
5 impurities since boron carbide does not introduce any foreign elements, and furthermore small changes in the stoichiometry are not significant/noticeable because the rare earth sites in $REB_{28.5}C_4$ have partial occupancies to begin with.

This motivated us to further re-examine the synthesis of Y_{1-}
10 $_xB_{28.5}C_4$ and after numerous tuning we were finally able to obtain "pure" $Y_{1-x}B_{28.5}C_4$ by a one-shot sintering method as described in the Experimental. SEM investigation of the "pure" $Y_{1-x}B_{28.5}C_4$ samples (Fig. 2(b)) shows no evidence of the secondary material with whitish contrast evident in
15 "conventional" $Y_{1-x}B_{28.5}C_4$. A further interesting feature is that the surface morphology of "pure" and "conventional" Y_{1-} $_xB_{28.5}C_4$ are quite different. "Conventional" $Y_{1-x}B_{28.5}C_4$ shows roundish grains while the "pure" material is formed of more angular longish rods. The difference in morphology is likely
20 due to the multiple grinding and sintering process for "conventional" $Y_{1-x}B_{28.5}C_4$ versus the one-shot synthesis for "pure". Considering the layered crystal structure of Y_{1-} $_xB_{28.5}C_4$ the anisotropic shape of natural growth is not inconsistent.

25 From XRD analysis the lattice parameters are determined to be a = 5.6432(7) Å, c = 56.897(7) Å and a = 5.6464(5) Å, c = 56.911(5) Å for "conventional" and "pure" $Y_{1-x}B_{28.5}C_4$, respectively, being well in agreement with the possible different content of yttrium in the samples. The XRD pattern
30 of the 'pure' sample does not contain reflections of binary boron carbide, but a small admixture of other yttrium borocarbonitrides in the homologous series is hard to exclude completely due to the strong similarity of the diffraction pattern of all the compounds belonging to this family.
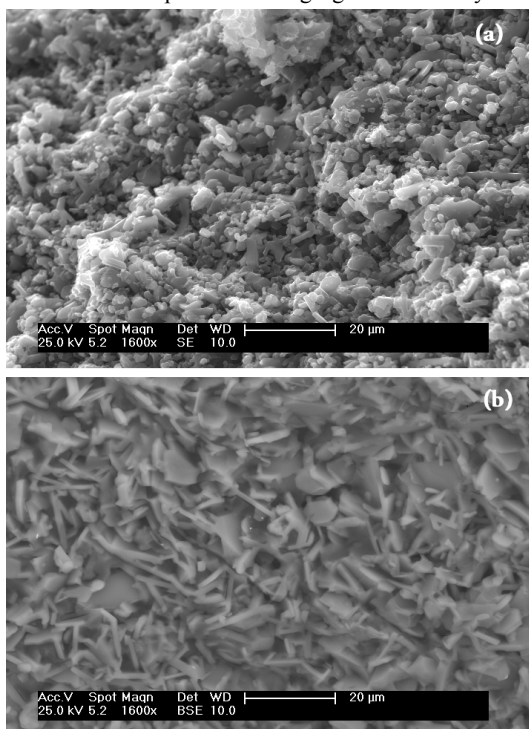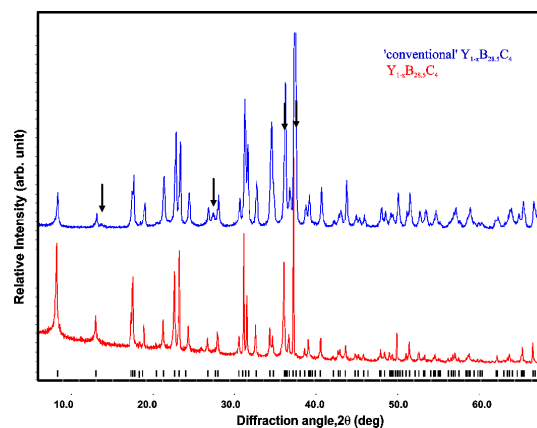
The Seebeck coefficients α of "conventional" and "pure" $Y_{1-x}B_{28.5}C_4$ are shown in Fig. 4. A striking difference was observed. α for "conventional" $Y_{1-x}B_{28.5}C_4$ is positive and
45 increases with increasing temperature, reaching a value ~73 μV/K at the highest temperature 1050 K, which is similar to the ~69 μV/K previously reported [32]. However, for the new nominally "pure" $Y_{1-x}B_{28.5}C_4$, the Seebeck coefficient is negative, increasing in absolute value as the temperature
50 increases from low temperature. Similar behavior was found for the other rare-earth borocarbonitrides [32,33]. However, α reaches a negative maximum around -27 μV/K below 200 K and gradually increases at higher temperatures. This behavior is detrimental to thermoelectric performance and it can be
55 surmised that there are undetectable traces of boron carbide which are affecting the Seebeck coefficent. This overall result is interesting since it shows the strong effect that boron carbide can have in shifting the Seebeck coefficient toward positive values. And it also might explain the reason why the
60 negative Seebeck coefficients of the other rare earth borocarbonitrides are also relatively small in absolute values compared to other boron cluster compounds with comparably large resitivity values. To develop these n-type boron cluster compounds further as the applicable counterpart for p-type
65 boron carbide, these results indicate it is very important to somehow find a way to remove all traces of boron carbide completely from the materials. In terms of conventional solid state reaction methods, in our opinion the synthesis has been pretty much optimized as feasible, and radically different
70 methods of synthesis like wet techniques or post-synthesis treatments need to be explored further.

To summarize, the Seebeck coefficient results, "pure" $Y_{1-x}B_{28.5}C_4$ was shown to exhibit n-type behavior, contrary to the p-type behavior which was previously reported. In the
75 homologous series, $Y_{1-x}B_{15.5}CN$ and $Y_{1-x}B_{22}C_2N$ had n-type behavior while the limit with no metal layers (Fig. 1), i.e. boron carbide, had strong p-type behavior. Being the most metal-poor compound, it was initially thought reasonable that

$Y_{1-x}B_{28.5}C_4$ might exhibit p-type behavior approaching boron carbide, but now it is revealed that even for a metal-poor boron cluster compound such as $Y_{1-x}B_{28.5}C_4$ (or with the yttrium partial occupancy explicitly expressed; $Y_{0.83}B_{28.5}C_4$)
5 n-type can be exhibited. This is discussed in the final section together with calculations on the rare earth boorcarbonitrides.
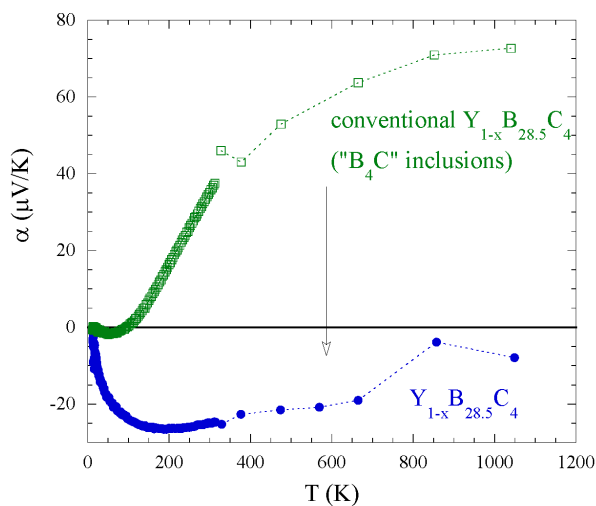
Figure 4: Temperature dependence of the Seebeck coefficient of "conventional" and "pure" $Y_{1-x}B_{28.5}C_4$.

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The transport properties (electrical resistivity and thermal conductivity) of "pure" $Y_{1-x}B_{28.5}C_4$ are shown in Fig. 5. Although the densities of samples are only ~65% it can give us some idea of the properties. The transport properties of "conventional" Y_{1-}
15 $_xB_{28.5}C_4$ showed varying results for different samples and we do not discuss them here because of the wide variation of factors due to the secondary phase of boron carbide, different morphologies, and densities. Regarding the properties of "pure" $Y_{1-x}B_{28.5}C_4$, the thermal conductivity shows a bad connection between the low
20 temperature and high temperature regions, but we think this is due to the well-known error in the TTO PPMS measurements at higher temperatures related to radiative losses in the interior of the apparatus which leads to overestimation notably above 200 K. The high temperature thermal conductivity takes values below 2
25 $Wm^{-1}K^{-1}$ which is within the range of 1.5 to 4.0 $Wm^{-1}K^{-1}$
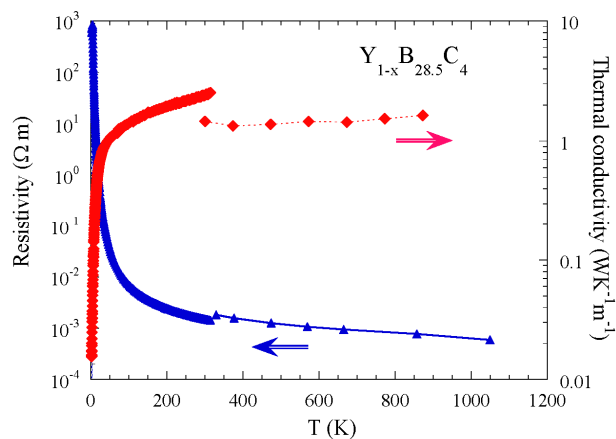
Figure 5: Temperature dependence of resistivity and thermal conductivity of "pure" $Y_{1-x}B_{28.5}C_4$.

observed for rare earth borocarbonitride samples with varying densities [32,33]. The resistivity of "pure" $Y_{1-x}B_{28.5}C_4$ shows
30 relatively small values with a minimum below 10^{-3} Ωm, which is quite good considering that the density is only ~65%. Previously we have observed that increasing the density from ~50% to ~75% for $Y_{1-x}B_{22}C_2N$ yielded an improvement in the electrical conductivity by close to two orders of magnitude and overall
35 increase in *ZT* of ~40 % due to the densification [33]. Actually, the resistivity of "pure" $Y_{1-x}B_{28.5}C_4$ with density of ~65% shown in Fig. 5 is smaller than observed for any of the non-doped rare earth borocarbonitrides, even SPS samples of $Y_{1-x}B_{22}C_2N$ with density of ~75%. This may indicate that the one shot synthesis
40 and the rod-like morphology or connection between grains is advantageous for electrical conductivity compared to the multiple sintering and round grains.

In any case, the low density of the measured specimen indicates there is still room to improve the thermoelectric
45 properties, however, due to the strong damping of the negative values of the Seebeck coefficients assumedly due to residual boron carbide, the ZT values of the present samples are very small being below 10^{-3}. While developing effective densification processes are important, it is now clear that finding a way to
50 remove boron carbide content of the materials even further, will now be the utmost priority in their further development as long awaited n-type counterparts to p-type boron carbide.

In total the chemical bonding in $Y_{1-x}B_{28.5}C_4$ can be described as a covalently bonded network polyanion $[B_{28.5}C_4]$ with the Y
55 cationic species embedded into the cavities of the polyanion. This picture is very similar to the one observed in direct space analysis with electron localizability tools for cage compounds like clathrates [43-46] or skutterudites [47,48], revealing different interactions within the polyanion (mostly covalent) and between
60 the polyanion and the filler atoms (mostly ionic). Assuming two electrons for each outer B-B bond and *closo* type of the B_6 group (according to Wade-Mingos rules [49,50]) with the homolytic cleavage of the electron number for the outer B-B bonds, one obtains demand of 20 electrons per $[B_6^{2-}]$ species. According to


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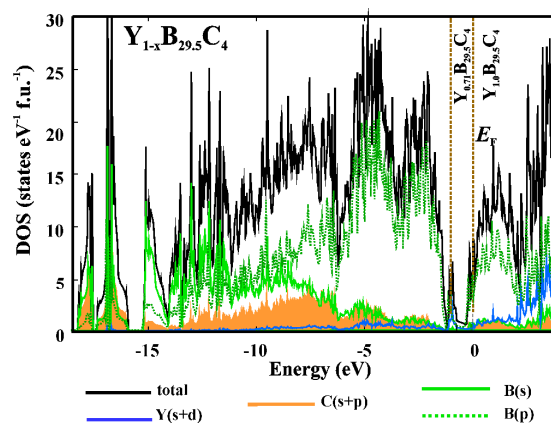
Figure 6: Calculated electronic density of states for $Y_{1-x}B_{29.5}C_4$ model. Total DOS (black) in comparison with the orbital resolved contributions of yttrium, boron and carbon. Fermi level

position is shown for different compositions within the rigid-band approximation.

the Wade-Mingos rules, the electron demand for this $[B_{12}^{2-}]$ *closo* species is 38. One formula unit of $Y_{1-x}B_{28.5}C_4$ for x = 0 represents a half of $(B_6)^{2-}$ group, two $(B_{12})^{2-}$ groups, an two $(CBC)^{3-}$. Assuming the two-centre-two-electron C-B and exo B-B bonds and Wade-Mingos rules as shown above an assumed total formula can be written as

$$[Y^{3+}][(B_6)^{2-}]_{0.5}[(B_{12})^{2-}]_2[(CBC)^{3-}]_2 \times 8p^+$$
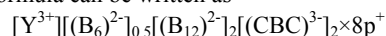
revealing a totally charge unbalanced situation. In order to obtain a balanced situation, the electronic demand within the $B_{28.5}C_4$ network should be smaller than expected from even applying Wade-Mingos electron counting, which itself allows to save more electrons compared to e.g. within the Zintl concept [51]. This illustrates again the peculiar bonding in boron cluster compounds.

The total electronic density of states for the $Y_1B_{29.5}C_4$ model shows a pseudo gap-like picture with the Fermi level located above the pseudo gap on the very steep edge of DOS (Fig. 6). The separated DOS double-peak at energy below -15.5 eV is formed by C(*s*) and B(*s*) states. Three DOS peaks between -15 and -6 eV are formed by C(*s*), C(*p*), B(*s*) and B(*p*) states representing the boron-carbon interaction. The large region with high DOS values between -6 eV and the Fermi level is mainly formed by *p* states of boron and carbon with the according s states contributions which decrease with the increasing energy, as well as the small contributions of the Y(*s*) and Y(*d*) states. This region visualizes the covalent interaction within the $[B_{29.5}C_4]$ network. The Y(*d*) states participate in small amounts in this interaction.

Pseudo gap-like structures are advantageous for thermoelectrics because of the sharp features around the Fermi level and indicate that this system should be developed further with doping to try to precisely control the filling around the Fermi level. Determining the sign of the Seebeck coefficient depends on the exact filling of the compound, whether the Fermi level is on the edge of the valence band for example or on the uptake in the pseudo gap, but the n-type characteristics indicate the latter. The calculations for $Y_{1-x}B_{29.5}C_4$ show that a pseudo gap-like structure in the DOS originates mainly from the covalent borocarbide network. The position of the Fermi level with x = 0.29 on the DOS branch with $\delta DOS/\delta E > 0$ reflects very much the negative Seebeck coefficient observed experimentally. Therefore, the fact that it was revealed that "pure" $Y_{1-x}B_{28.5}C_4$ is actually n-type and not p-type as previously thought (as it is the most metal-poor in the series) is reasonable. Nevertheless, the same feature may be obtained for x = 0 (cf. Figure 6). Thus the correct prediction of the thermopower sign depends on the filling extent in $Y_{1-x}B_{28.5}C_4$ on the one hand and in the shape of DOS in vicinity of the Fermi level. The latter may be influenced by the partial disorder in the crystal structure. The study of the latter feature is ongoing.

Conclusions

Boron cluster compounds are prospective systems as high temperature thermoelectric materials. The rare earth borocarbonitrides, $RB_{15.5}CN$ and $RB_{22}C_2N$ were previously found to exhibit the first instances of intrinsic n-type behavior in boron icosahedra compounds, and are interesting as potential counterparts to boron carbide which is one of the few thermoelectric compounds with a history of commercialization. These compounds are in a homologous series and it was previously reported that the most metal-poor compound $Y_{1-x}B_{28.5}C_4$ was p-type. In this work we discover that $Y_{1-x}B_{28.5}C_4$ samples actually contain boron carbide inclusions. In comparison to that of previous small flux-grown single crystals, a metal-poor composition in the synthesis was found to be effective in preventing the formation of these boron carbide inclusions, and "pure" $Y_{1-x}B_{28.5}C_4$ is actually n-type. The boron carbide inclusions had a large effect on the Seebeck coefficients. There are also indications that undetected amounts of boron carbide may be capping the n-type behavior in the rare earth borocarbides, and it is important to further find ways to remove boron carbide traces from the samples. Calculations on $Y_{1-x}B_{28.5}C_4$ as a representative of the rare earth borocarbides, show that a pseudo gap-like structure exists in the density of states around the Fermi level which mainly originates from the covalent borocarbide network. Pseudo gap-like structures are advantageous for thermoelectric properties and precise filling control in these compounds should be investigated further.

Notes and references

a National Institute for Materials Science (NIMS), Materials Nanoarchitechtonics Center (MANA), Namiki 1-1, Tsukuba 305-0044, Japan. Fax: +81-298516280; Tel:+81-298604323; E-mail: MORI.Takao@nims.go.jp
b Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennoudai, Tsukuba 305-8671, Japan
c Hiroshima University, Kagamiyama 1-3-2, Higashi-Hiroshima 739-8511, Japan
d Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany. Fax: +49 (351) 4646 4002; Tel: +49 (351) 4646 4001; E-mail: Juri.Grin@cpfs.mpg.de

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Graphical abstract of Article "Origin of the n-type behavior in rare earth borocarbide $Y_{1-x}B_{28.5}C_4$", Takao Mori et al., submitted to the Dalton Transactions themed issue on Inorganic Chemistry for Renewable Energy Conversion and Storage.

Investigations were carried out on $Y_{1-x}B_{28.5}C_4$ which is the compound with least metal content in a series of homologous rare earth borocarbonitrides, which have been attracting interest as high temperature thermoelectric compounds because they can embody the long awaited counterpart to boron carbide. It was revealed that the presence of boron carbide inclusions was the origin of the p-type behavior in the Seebeck coefficient α previously observed for $Y_{1-x}B_{28.5}C_4$ in contrast to $Y_{1-x}B_{15.5}CN$ and $Y_{1-x}B_{22}C_2N$. Counterintuitively, a metal-poor mixture in the synthesis successfully yielded $Y_{1-x}B_{28.5}C_4$ samples apparently free of boron carbide inclusions. "Pure" $Y_{1-x}B_{28.5}C_4$ was found to exhibit the same anomalous and attractive n-type behavior found for the other rare earth borocarbonitrides even though it is at the boron-rich end. Calculations reveal a pseudo gap-like structure in the density of states and the importance of the borocarbonitride network.