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Zr doped *β*-rhombohedral boron: widely variable Seebeck coefficient and structural properties

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Abstract

The doping effect of zirconium on the structure, Seebeck coefficient and electrical resistivity of *β*-rhombohedral B was studied for the metal rich concentration range Zr_xB_{100-x}, 1.88≤x≤2.75. Structural studies proved the Zr atoms mainly in *E* and *D* voids for the metal rich compositions, and also elucidated the minor Zr occupancies of the *N*, *F* and A_1 holes. Seebeck coefficients were effectively shifted within a wide range of positive and negative values by varying the Zr content (*p*-type: S_{max} ~ +420 μVK^{-1} at 673 K for x=1.88; *n*-type: S_{max} ~ -670 μVK^{-1} at 473 K for x=2.74). Electrical resistivities generally followed the Mott's relation for the variable-range hopping. Excellent compositional agreement has been observed between structural and thermoelectric properties discontinuities.

Keywords: *β*-rhombohedral boron; Zr-doping; *p*/*n* transition

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1. Introduction

Boron and borides are considered to be promising thermoelectric (TE) materials for use at high temperatures of more than 1300 K [1-6], however, their properties still need to be developed further to enable practical use. Regarding elemental boron, the structure of *β*-rhombohedral (*β-rh*) B (space group $R\overline{3}m$) [7-11] has been extensively studied with respect to its ability to accommodate interstitially different kinds of foreign atoms [12-14]. It has been shown that metal doping into *β-rh* B can control the bonding nature in and between the clusters, delivering variation of physical properties such as electrical and thermal conductivities and Seebeck coefficient [13,15-20]. The interstitial doping of *β-rh* B by certain 3*d*-metals (*e.g.* V, Cr, Fe, Ni, Cu) led to negative values of TE power in the originally *p*-type semiconducting material in certain temperature ranges [13,21]; the structural and electronic properties of some solid solutions (i.e. V:B, Fe:B, Cu:B) have been consistently studied by different research groups [13,15,22,23].

Information on physical properties of larger *d*-metals *β-rh* B solid solutions is scarce. A partial crystal structure of Zr-doped *β-rh* B exhibiting the formula $ZrB_{\sim 51}$ has been reported in the late seventies from powder X-ray diffraction data within a series of works mainly focused on elucidation of details on positional and occupancy parameters of transition metal atoms in the cavities of the boron lattice [24]. Later on [12] detailed structure analysis has been made for Zr sites distribution in the *β-rh* B crystal with Zr:B ratio 1:143, exhibiting as low dopant content as ~0.69 at.%. Both studies showed different results regarding dopant atom site preferences, however they are evidence of rather high solid solubility of such a large transition element in *β-rh* B. Contrasting data are available for the TE properties of Zr-doped *β-rh* B showing highly positive (for $Zr_{1.0}B_{105}$ and $Zr_{0.8}B_{105}$ [18,25]), and slightly negative (for $Zr_{1.0}B_{105}$ [26]) values of Seebeck coefficient in the temperature ranges 200 K - 300 K and 300 K - 500 K respectively. In view of these inconsistencies and since the structure determination from powder diffraction data of $ZrB_{\sim 51}$ was only of a rather preliminary nature, in the current study we i) aimed to clarify the structure of metal rich Zr-doped *β-rh* B including the details of boron atom framework and dopant sites preferences as well as we ii) undertook the task to shed a light on the TE properties and their compositional dependence within the studied solubility range.

2. Experimental procedure

2.1. High temperature synthesis (HTS)

The proper weight ratios of amorphous boron (3N, SB-Boron Inc., USA) and zirconium oxide (3N, Koujundo Kagaku Co., Japan) were well mixed in mortars and compacted by cold iso-static pressing into cylindrical bars applying pressure of 300 MPa. The compacted rod was placed in a crucible made from sintered BN which was inserted into a graphite susceptor. The reaction process was performed under dynamic vacuum at a predetermined temperature of about 2073 K – 2173 K for 4 h -8 h using a radio frequency (RF) induction furnace; afterwards the setup was cooled down in 1h to room temperature. After synthesis, the samples were substantially surface cleaned, powderized, compacted and annealed for 4 h at 1973 K.

2.2. Spark plasma sintering (SPS)

For SPS, each sample was pulverized in a mortar to μm-size of particles, inserted in a 10 mm graphite die and set in the middle of the spark-plasma chamber of a Dr. Sinter 1080 apparatus (Fuji Denpa Kogyo Inc.). The sintering was performed after evacuating the chamber and afterwards filling with Ar to 1 atm. The maximum applied pressure, temperature and holding time were 60 MPa, 1923 K and 5 min respectively.

2.3. Single crystal X-ray diffraction (XRD)

Single crystals were isolated from the fragmented melted portions of $ZrB_{\sim 45}$ samples. Single crystal XRD data were collected on a Bruker APEX II diffractometer (CCD detector, κ-geometry, Mo Kα radiation) (single crystal I). Orientation matrix and unit cell parameters were derived with the help of the program DENZO; multi-scan absorption correction was applied using the program SADABS; frame data were reduced to intensity values applying the SAINT-Plus package [27,28]. Alternatively, a different crystal (single crystal II) was measured with a four-circle diffractometer Rigaku AFC 7R. The Laue symmetry and unit cell dimensions were determined from the measurements and least square refinement of 25 reflections centered in the range $8 \leq 2\theta \leq 50$; the absorption correction was performed applying azimuthal scan (ψ-scan) method [29]. Possible space groups were found out from the analysis of systematic absences performed with the help of program ABSEN [30,31]. The structures were solved by direct methods and refined with the SHELXS-97 [32] and SHELXL-97 [33] programs, respectively. The atom coordinates were standardized with the program STRUCTURE TIDY [34]. Further details concerning the single crystal XRD experiments and data refinement are summarized in Tables 1-2.

2.4. Powder XRD

The phase compositions of the reacted products were verified from powder XRD data using a standard high-resolution powder X-ray diffractometer (R-2000, Rigaku Co.) with Cu$K\alpha$ radiation. The structural details have been studied from the samples obtained after TE properties measurements. Structure refinements were performed from powder X-ray intensity data collected in the range $3° \leq 2\theta \leq 110°$ (120°) with the scanning step width 0.02° and sampling time 15 sec/step with full-profile Rietveld method using the program FULLPROF [35] applying the initial atomic positions obtained from the single crystal XRD data.

2.5. TE properties measurements

For thermoelectric properties measurements, the samples were additionally heat treated for about 2 hours at 873 K in He atmosphere in the ULVAC ZEM-2 equipment. Resistivity and TE power were measured from cut bar-shaped (in general about 5 mm ×5 mm ×8 mm) HTS and SPS samples by using the four probe method and differential method respectively.

3. Results and discussion

3.1. Structure refinement from single crystal XRD data

The space group $R\bar{3}m$ classically used for the refinement of *β-rh* B structure was found to be compatible with the observed extinction rules for both sets of single crystal intensities data. Two Zr and several B atom sites were determined with direct methods; the remaining atom sites were localized from analysis of the difference-Fourier maps revealing the structure model exhibiting in total 15 atom positions of B and 2 atom sites of Zr (recognized as commonly denoted D and E voids). In further description the boron sites have the same notation as that used in Refs. [7,12]. No additional B atoms (B16-B20) between the B_{12} icosahedra such as were observed in the 20-atom position's *β-rh* B structure [7] and in the structures of $ZrB_{\sim51}$ [24] and $Zr_{0.72}B_{105}$ [12], were found in the current crystals. In agreement with the results of previous studies on the crystal structures of Zr-, Mg- and Sc-doped *β-rh* B, the peaks of residual electron densities were observed in the sites F (0.59 $e^-/Å^3$ in 18*g*, x=0.38), N (0.57 $e^-/Å^3$ in 18*h* $(x,\bar{x},z)$, x=0.787, z=0.090) (crystal I) and A_1 (1.08 $e^-/Å^3$ in 6*c*, *z*=0.36), *F* (0.96 $e^-/Å^3$ in 18*g*, *x*=0.38) (crystal II). Although the refinement of site occupancy parameters assuming the population of these voids by Zr rendered rather low values (Table 2), the accounting for atoms in *F*, *N* and A_1 sites led, similarly to other metal-doped icosahedral borides [36-38], to a significant improvement of the reliability factors and to a substantive decrease of the remaining residual electron densities in the Fourier density maps. The refinements of occupancies of the atom sites rendered the range of metal:boron ratios close to 1:40 -1:41 which is significantly higher as compared to the Zr/B ratios reported previously [12,24]. Refined positional and displacement parameters, and site occupation factors are given in Tables 1-2 and Table 1 in Supporting Information; selected interatomic distances are listed in Table 2 Supporting Information.

Table 1. Crystallographic data for Zr doped *β-rh* B ($R\bar{3}m$; No.166; Z=3).

Compound	$ZrB_{41.101}$ (crystal I)	$ZrB_{39.967}$ (crystal II)
Formula from refinement	$Zr_{2.5014}B_{102.809}$ ($Zr_{7.5042}B_{308.4264}$)	$Zr_{2.58}B_{103.116}$ ($Zr_{7.74}B_{309.348}$)
Nominal composition	$Zr_{2.375}B_{97.625}$	$Zr_{2.441}B_{97.559}$
Lattice parameters [Å]	a=10.9363(5), c=24.0253(10)	a=10.939(1), c=24.029(6)
Volume [$Å^3$]	2488.5(1)	2490.0(9)
ρ_{calc} [g/cm^3]	2.681	2.703
Diffractometer	Bruker APEX II, MoKα	Rigaku AFC 7R, MoKα
$2\theta_{max}$ [°]	59.98	63.98
N(hkl) measured	11318	10704
N(hkl) unique	890	1099
N(hkl) observed ($F_{hkl}>4\sigma(F)$)	669	449
Refined parameters	115	108
Reliability factors	$R_F^2 = \Sigma \vert F_o^2-F_c^2 \vert / \Sigma F_o^2=0.036$	$R_F^2 = \Sigma \vert F_o^2-F_c^2 \vert / \Sigma F_o^2=0.054$
	GooF=0.990	GooF=0.796
Extinction coefficient	0.000(1)	0.000(6)
Residual electron density [$e^-/Å^3$] (max; min)	+0.46; -0.37	+0.70; -1.40

3.2. Structure description

The structure of *β-rh* B exhibits two kinds of icosahedral boron atom networks alternating along the *c* direction [39] (Fig. 1). The networks of type II icosahedra which are composed of B1, B2, B7 and B9 and located at z=0, ⅓ and ⅔ can be seen as Kagomé 6363-nets. The nets appearing at z=1/6, 3/6 and 5/6 are formed by the groups of three face-fused icosahedra (type III; built by B3, B4, B8, B10, B11, B12, B13 and B14) with a general formula B_{28} and type I icosahedra (constructed of B5 and B6). The [B_{28}] clusters from different layers inter-link via boron atoms (B15 in 3*a* 0,0,0) in such a way that the [B_{28}] and [B_{12}] units are located below and above hexagons and triangles of the Kagomé 6363-nets. The tri-icosahedra are generally found with atomic defects on particular sites [9,40]; in case of *β-rh* B structure, the partial occupancy is well established leading, instead of [B_{28}], to the boron deficient actual formula. The structure exhibits several interstitial atomic positions which can accommodate boron or other atoms if partially occupied [7,12].

The refinement of occupancy parameters of partially occupied sites in Zr-doped *β-rh* B from powder XRD data [24] using the atom coordinates of Sc doped *β-rh* B structure [41] as the start values revealed the Zr:B ratio of ~1:51 (1.93 at% Zr) exhibiting 52.8%, 14.5%, 27.9%, 18.1% and 0.7% occupancy for B13 (18*h*), B16 (18*h*), Zr2 (18*h*, *D* void), Zr3 (6*c*, *E* void) and Zr4 (18*g*, 0.37,0,1/2, *F* void) respectively (a=10.9564 Å, c=24.0201 Å). Subsequent work [12] on the B-rich crystal reported three atom sites of Zr (in A_1, *D*, and *E* voids) displaying rather distinct from previous study, occupation percentages on both Zr (1.7%, 8.1% and 10.7% respectively) and B (62.5% for B13 and 35.8% for B16) atom sites which leads to as low dopant/boron ratio as 1:143 (0.69 at% Zr). Our single crystal XRD study results show that at ~2.4 at.% Zr doping level, the *D* and *E* voids are the main ones that are occupied by metal atom whereas the occupancies of other interstitial metal sites (*F*, *N* and A_1) are very small, ranging within 0.33%-0.7%.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters[a,b] (in [Å^2]) for Zr doped *β-rh* B as obtained from single crystal XRD.

Atom	$ZrB_{41.101}$	$ZrB_{39.967}$
B1 in 36*i* (*x,y,z*)	x=0.0008(2), y=0.1725(2), z=0.3249(1)	x=0.0012(4), y=0.1728(4), z=0.3247(2)
occ.; U_{eq}	1.0; 0.0071(4)	1.0; 0.0076(7)
B2 in 36*i* (*x,y,z*)	x=0.0144(2), y=0.3732(2), z=0.0378(1)	x=0.0140(4), y=0.3728(4), z=0.0379(1)
occ.; U_{eq}	1.0; 0.0064(4)	1.0; 0.0052(7)
B3 in 36*i* (*x,y,z*)	x=0.0445(2), y=0.2626(2), z=0.0821(1)	x=0.0450(4), y=0.2630(4), z=0.0823(2)
occ.; U_{eq}	1.0; 0.0066(4)	1.0; 0.0053(7)
B4 in 36*i* (*x,y,z*)	x=0.2520(2), y=0.0149(2), z=0.1534(1)	x=0.2517(4), y=0.0154(4), z=0.1535(2)
occ.; U_{eq}	0.9964(7)[c]; 0.0065(4)[d]	0.993(1)[c]; 0.0067(7)[d]
B5 in 18*h* $(x,\bar{x},z)$	x=0.3873(2), z=0.1100(1)	x=0.3876(3), z=0.1099(2)
occ.; U_{eq}	1.0; 0.0053(5)	1.0; 0.0058(7)[d]
B6 in 18*h* $(x,\bar{x},z)$	x=0.4173(1), z=0.1797(1)	x=0.4172(3), z=0.1796(2)
occ.; U_{eq}	1.0; 0.0039(5)	1.0; 0.0046(9)
B7 in 18*h* $(x,\bar{x},z)$	x=0.4417(2), z=0.0548(1)	x=0.4410(3), z=0.0550(2)
occ.; U_{eq}	1.0; 0.0065(6)	1.0; 0.0058(7)[d]
B8 in 18*h* $(x,\bar{x},z)$	x=0.5014(2), z=0.1937(1)	x=0.5017(3), z=0.1940(2)
occ.; U_{eq}	1.0; 0.0060(5)	1.0; 0.0066(9)
B9 in 18*h* $(x,\bar{x},z)$	x=0.5373(2), z=0.0659(1)	x=0.5374(3), z=0.0656(2)
occ.; U_{eq}	1.0; 0.0059(5)	1.0; 0.0061(9)
B10 in 18*h* $(x,\bar{x},z)$	x=0.5642(1), z=0.1347(1)	x=0.5642(3), z=0.1350(2)
occ.; U_{eq}	1.0; 0.0059(6)	1.0; 0.0066(9)
B13 in 18*h* $(x,\bar{x},z)$	x=0.6110(3), z=0.2766(2)	x=0.6104(5), z=0.2769(4)
occ.; U_{eq}	0.642(10); 0.013(1)	0.70(2); 0.014(2)
B11 in 18*h* $(x,\bar{x},z)$	x=0.7239(2), z=0.1604(1)	x=0.7238(3), z=0.1599(2)
occ.; U_{eq}	1.0; 0.0083(6)[d]	1.0; 0.0084(10)
B12 in 18*h* $(x,\bar{x},z)$	x=0.7570(2), z=0.2305(1)	x=0.7568(3), z=0.2307(2)
occ.; U_{eq}	1.0; 0.0058(6)	1.0; 0.0061(10)
B14 in 6*c* (0,0,*z*)	*z*=0.1151(2)	*z*=0.1157(4)
occ.; U_{eq}	1.0; 0.0058(9)	1.0; 0.0052(17)
B15 in 3*a* (0,0,0) occ.; U_{eq}	1.0; 0.018(2)[e]	1.0; 0.014(3)
Zr2 in 18*h* $(x,\bar{x},z)$ (*D*)	*x*=0.53595(4), *z*=0.34227(3)	*x*=0.53605(10), *z*=0.34248(7)
occ.; U_{eq}	0.299(2); 0.0072(3)	0.306(2); 0.0088(5)
Zr3 in 6*c* (0,0,*z*) (*E*)	z=0.26437(5)	z=0.26426(10)
occ.; U_{eq}	0.333(2); 0.0040(4)	0.345(4); 0.0043(7)
Zr44 in 18*g* (*x*,0,½) (*F*)	*x*=0.376(5)	*x*=0.385(7)
occ.; U_{eq}	0.0036(7)[c]; 0.0065(4)[d]	0.007(1)[c]; 0.0067(7)[d]
Zr11 in 18*h* $(x,\bar{x},z)$ (*N*)	*x*=0.785(3), *z*=0.092(3)	-
occ.; U_{eq}	0.0033(7); 0.0083(6)[d]	-
Zr77 in 6*c* (0,0,*z*) (A_1)	-	*z*=0.360(6)
occ.; U_{eq}	-	0.006(2); 0.0058(7)[d]

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor; [b] anisotropic displacement parameters are listed in Table 1 Supporting Information; [c] site occupancy factors have been constrained; [d] displacement parameters have been constrained to be equivalent for following groups of atoms: i) B4, Zr44; ii) B11, Zr11; iii) Zr77, B5, B7; [e] isotropic displacement parameter

The *D* void is large enough to accommodate the atoms of the first transition metal row, however it is rather small for Zr, delivering too short Zr2-B13 distances for full occupancy of both atom sites simultaneously (Table 2 Supporting Information). Similarly to the structure of Sc-doped *β-rh* B [41], the occupancy value of B13 site is close to ⅔ (64.2% and 70.0%) whereas the *D* void is filled for about 30% with Zr2. The information on *E* void occupancy is much less extensive than that for the *D* hole. Because of the large distance between the center of the hole to the neighboring atoms (*i.e.* 2.408(2) Å in pure *β-rh* B), the larger ions such as Li, Mg, Sc, Hf and Zr fit well into the *E* void and show high level of occupancy, e.g. full and almost full (91%) occupancy for Li [42,43] and Mg [44-46] respectively and 72.7% for Sc [41]. In comparison with Li, Mg and Sc dopants, the Zr exhibits rather medium degree of filling of the *E* void, 33.3%-34.5%. The adjacent A_1 void ($d_{\mathrm{Zr3\text{-}Zr77}}$=2.3 Å) remains almost unoccupied (Occ. Zr77 is 0.7%) exhibiting short Zr-B distances ranging within 2.07-2.24 Å; obviously A_1 hole is too small for Zr. Refinements of both single crystal data sets showed a very minor occupancy of the *F* site as well. Insertion of Zr in 18*g* (*x*,0,½) position (*F* site) leads to the partial replacement of two boron atoms (namely B4) of two neighboring [B_{28}] units by one metal atom at an intermediate position. Mixed B/metal atom occupancy of split icosahedral site has already been observed for some metal doped *β-rh* B structures [38, 44-46] including $ZrB_{\sim 51}$ [24] as well as more recently for other higher borides [36, 37]. Additionally, a new *N* void (18*h*) reported for the first time for Mg-doped *β-rh* B [44-46] was found to be populated for only 0.3% by Zr11 in one of the studied single crystals. Both *D* and *E* sites have 15 close boron neighbours (Fig. 1d,e); the Zr44 (*F* void), Zr11 (*N* void) and Zr77 (A_1 void) are surrounded by 10, 16 and 12 boron atoms respectively (Fig. 1f-h). The Zr-B distances range within 2.07 (Zr77-B1) and 2.62 (Zr11-B13) except the short distances for the B4/Zr44 atoms located in split atom position.

The boron networks of Zr doped *β-rh* B (Fig. 1b,c) agree closely with that of *β-rh* B [7], however the interstitial atoms B16-B20 situated in a partially occupied positions in un-doped *β-rh* B have not been detected in current single crystal study thus revealing the structure with only 15 B atom positions. Further, alike in ScB_{28} [41], $ZrB_{\sim 51}$ [24] as well as more recently in Mg-doped *β-rh* B structures [44-46], the B4 site shows slight under-occupation in both crystals.

The B-B distances within the icosahedra cover the range 1.710 Å (1.706 Å) (B6-B6, icosahedron type I) – 1.896 Å (1.892 Å) (B3-B3, icosahedron type III) in single crystals I and II respectively; the shortest contact distance decreases upon doping in comparison with corresponding B-B distance in the structure of 20-atom positions' *β-rh* B ($d_{B6\text{-}B6}$=1.75 Å [7]). Alike in other icosahedral borides, the B-B distance between icosahedra in Zr-doped *β-rh* B structure are shorter than the B-B distances within icosahedra. The icosahedron I exhibits shorter B-B contact distances as compare to B_{28}-unit and icosahedron II showing the values between 1.710 Å - 1.771 Å / 1.706 Å - 1.782 Å vs 1.736 Å - 1.896 Å / 1.735 Å - 1.892 Å and 1.803 Å - 1.880 Å / 1.815 Å - 1.876 Å (in single crystal I / single crystal II respectively). The distance between B13 atoms, at which the icosahedra condense into B_{28}-unit (1.828 Å / 1.848 Å), is also significantly shorter if compared to the B13-B13 bond length in *β-rh* B (1.898 Å).

3.3. Dopant atom site preferences from powder XRD data

Powder XRD patterns of Zr_xB_{100-x} ($1.88 \leq x \leq 2.76$) recorded after heat-treating procedure for all samples exhibited the spectrum of metal-doped *β-rh* B structure. Examination of intensity distribution within the series of diffractograms spotted out the liability of different site occupancies by Zr atoms depending on metal content of the sample; this supposition was further confirmed from Rietveld refinements (Table 3, Fig. 2). The structure models obtained from single crystal X-ray diffraction studies presented above were used for Rietveld refinements of powder data; the *D*, *E*, *F*, *N* and A_1 doping sites were selected for the refinements of Zr occupancy. The B16 atom site appeared to be populated only in the sample with higher B content, while the occupancies of *N*, *F* and A_1 void were found to be very small within the entire investigated concentration range in good agreement with the results of single crystal structural studies (Tables 2-3). With respect to refinement procedure, we should note that introduction of Zr into the *F*, *N*, and A_1 voids in the starting atom model followed by further refinement of positional and occupancy parameters improves significantly the final reliability factors despite small filling percentage of corresponding atom sites. In good correspondence with single crystal results, the occupancy of D site does not exceed 30%; starting from about 17% at 1.88 at.% Zr, the occupancy of *D* site rapidly increases and saturates above 2.4 at% Zr (Fig. 3). In contrast, the occupancy of *E* site increases rather moderately towards higher Zr content. Both *D*- and *E*-site occupancy *vs*. Zr content dependencies show noticeable anomalies upon reaching *ca* 2.58 at.% Zr; the increase of Zr content within $Zr_{2.58}B_{97.42}$- $Zr_{2.75}B_{97.25}$ interval is mainly realized via increased population of *F*-, *N*- and A_1- sites (Table 3). In compliance with the features of atom sites occupancies, the lattice parameters *vs*. Zr content dependencies show anomalies above 2.58 at.% (Fig. 4). Further doping (above 2.75 at.% Zr) was not effective at our synthesis conditions due to considerable precipitation of secondary ZrB_{12} phase, particularly in the SPS sintered samples.

Table 3.

Compositions, lattice constants and occupancies of partially occupied atom sites in the Zr-doped *β-rh* B (space group $R\bar{3}m$) as obtained from Rietveld refinements of powder XRD data[a,b] in comparison with the results obtained from single crystal XRD data refinements and literature data.

Composition (at. %)	Lattice parameters (Å) a	c	Atom site occupancy (%) 18*h* (Zr, *D*)	6*c* (Zr, *E*)	18*g* (Zr, *F*)	18*h* (Zr, *N*)	6*c* (Zr, A_1)	18*h* (B16)	Comments
$Zr_{0.69}B_{99.31}$	10.932	23.849	8.1	10.7			0.17	35.8	[12]
$Zr_{1.96}B_{98.04}$	10.9564	24.0201	27.9	18.1	0.7		-	14.5	[24]
$Zr_{1.88}B_{98.12}$	10.9492(9)	23.939(2)	16.8	32.8	3.4	1.6	-	14.1	HTS, powder
$Zr_{2.37}B_{97.63}$	10.9363(5)	24.025(1)	29.9	33.3	0.4	0.4	-	-	HTS, SC
$Zr_{2.44}B_{97.56}$	10.938(1)	24.029(6)	30.6	34.5	0.7	-	0.6	-	HTS, SC
$Zr_{2.38}B_{97.62}$	10.9395(7)	24.007(2)	25.7	38.2	1.9	1.3	0.2		SPS, powder
$Zr_{2.58}B_{97.42}$	10.9382(6)	24.002(2)	26.9	40.8	2.7	1.9	-	-	SPS, powder
$Zr_{2.60}B_{97.40}$	10.9449(6)	24.027(2)	27.6	36.8	3.1	2.3	0.8	-	SPS, powder
$Zr_{2.74}B_{97.26}$	10.9425(7)	24.028(2)	27.0	40.7	3.9	3.5	-	-	HTS, powder
$Zr_{2.75}B_{97.25}$	10.9404(6)	24.032(2)	27.9	42.2	3.6	2.4	-	-	HTS, powder

[a] Occupancy of B13 (18*h*, $x,\bar{x},z$) was fixed to 60% for all samples; [b] occupancy of B4 (36*i*, x,y,z) was fixed to determined value upon the refinement of occupancy of Zr in 18*g* (*F* site)

3.4. Electrical resistivity

In general two mechanisms exist to describe the transport properties of lightly doped semiconductors, Mott's model for the variable-range hopping-type (VRH) resistivity [47] and phonon-assisted hopping conduction model of Emin and Holstein [48]. Both models have been found appropriate for a large number of materials, from piezoelectric semiconductors to graphene nanotubes. The dependence of resistivity for Zr-doped *β-rh* B in the temperature region from 323 K to 873 K is shown in Fig. 5 on a logarithmic scale against $T^{-1/4}$ in concord with the literature data on conductivity of *β-rh* B doped with other transition metals. Regardless of the Zr content, the resistivity plots in the chosen representation are following linear dependencies in agreement with the Mott's model for the variable-range hopping-type resistivity,

$$\rho = \rho_0 \exp\{\left(\frac{T_0}{T}\right)^{1/4}\}, T_0 = \frac{60\alpha^3}{\pi N(E_f)k_B}$$

where ρ_0 is a constant, T_0 is Mott's characteristic temperature, α^{-1} is the localization length of the wave function of the carriers, $N(E_f)$ is the density of states on the Fermi level and k_B is the Boltzmann constant. The value of electrical resistivity increases following the increase of Zr content until it saturates at 2.60 at.% Zr, notwithstanding differences in density of materials (relative densities in general varied as ~50% and ~80% for HTS and SPS samples respectively). The resistivity of the samples at low temperatures varies greatly (up to 3 orders) depending on Zr concentration; for Zr-rich samples, large decreases of the resistivity were observed with increase of the temperature.

The analysis with a phonon-assisted hopping conduction model,

$$\rho = \frac{T}{C}\exp\{\frac{k_B T}{E}\},$$

(C is a constant and E is the activation energy of mobility) was found to be inappropriate for the samples studied in current work.

3.5. Thermopower

Fig. 6 shows the variation of the Seebeck coefficient with temperature for various samples. Considering the analysis of resistivity one should expect the Seebeck coefficient to behave in agreement with VRH model, and thus follow the equation proposed by Brenig et al. (1973) [49]

$$S \approx \frac{k_B^2}{64q} T_0^{1/2} T^{1/2} \{N'(E)/N(E)\}_{E_f} \{1 + (T_0/T)^{1/4}\},$$

where q is a charge of carriers and T_0 is a constant inverse proportional to $N(E_F)$ and E is the thermal activation energy of the mobility of carriers. More simple relations of $\mathrm{S} \propto (\mathrm{T_0 T})^{1/2} d(\ln\mathrm{N(E)})/d\mathrm{E}|_{\mathrm{E_F}}$ was proposed by Zvyagin [50], while $S \sim T^{1/2}$ was proposed by Overhof [51]. In case if the phonon-assisted hopping-type conduction is dominant, the Seebeck coefficient tends to be proportional to the temperature

$$S = \frac{(T\Delta S' + E_T)}{qT} = A + BT \, ,$$

where A and B are constants, $\Delta S'$ is the change in entropy due to the insertion of a carrier, E_T is the average vibrational energy, and q is the charge of carriers. However, the experimental results obtained for the Zr doped *β-rh* B do not completely follow any of the described models. While the *p*-type samples demonstrate a maximum of Seebeck coefficient in the range around 700 K, the *n*-type samples clearly demonstrate a minimum in the medium temperature range. Similar behavior is explained for a V-doped *β-rh* B as a result of the combined influence of VRH conduction and band conduction [52]. In case of Zr-doped *β-rh* B we can state that the behavior of different carrier types should be considered from the point of view of different models.

Thus far, the TE properties have been studied for the boron rich $\mathrm{Zr_xB_{100-x}}$ samples (x<1) in the temperature range 200-300 K [18]. In agreement with previous studies, our boron-rich Zr-doped *β-rh* B samples up to x≤2.38 ($\mathrm{Zr_{1.88}B_{98.12}}$ - $\mathrm{Zr_{2.38}B_{97.62}}$) showed high positive values of thermoelectric power (Fig. 7). Towards higher Zr content, the sign of Seebeck coefficient shifts from positive to negative values reaching the extraordinary high negative values (almost -670 $\mu\mathrm{VK^{-1}}$ at 473 K) for 2.74 at% Zr-doped *β-rh* B. This is the first evidence of such high negative thermopower of transition metal solid solutions in *β-rh* B.

4. Summary

Up-to-now, very few transition metal dopants were reported to evoke negative Sebeck coefficients in *β-rh* B at ambient conditions, i.e. V, Cr, Fe and Ni [13]. The TEP temperature dependence of Zr doped *β-rh* B is qualitatively similar to that in B:V and B:Fe. Considering the literature data on Zr-poor *β-rh* B (about 600 μVK^{-1} for $Zr_{0.94}B_{99.06}$ at 300 K [18]), a certain reduction of thermopower values takes place at lower Zr contents (<1.88 at.% Zr), but Seebeck coefficients remains positive, moderately decreasing up to ~2.4 at.% Zr where a steep change to negative values occurs. The jump is considerably larger than that in B:Fe, while the amounts of doped metal at the crossover from positive to negative TEP values are comparable in both Zr and Fe solid solutions. The data for *n*-type Fe-doped *β-rh* B as well as for *n*-type Zr-doped *β-rh* B indicate a sign reversal to positive values at high temperatures. According to structural studies, the dopant atoms distributions in two structures are different. Fe atoms in the *β-rh* B structure are accommodated in the interstitial sites A_1 and *D* only [13,21,52,53]. In both sites, the occupancy increases linearly with the Fe content and the variation of the lattice parameters does not show significant anomalies. From an electronical point of view, the *p-n* transition is accompanied by a correlation among the diluted Fe atoms generating a specific system of electronic states in the band gap [13]. When a critical value of this correlation is crossed, the quality of electronic transport changes abruptly. In more recent work, the origin of the *p-n* crossover was attributed to the certain changes in crystalline structure which might be restricted to the details of structural elements according to the analysis of the phonon spectra [21]. In contrast, the dopant atoms in Zr-doped *β-rh* B are distributed within two major sites, *E* and *D*. Our careful single crystal studies elucidated three more sites (*F*, *N*, and A_1) available to accommodate minor quantities of Zr. Both lattice parameters and major dopant atom sites occupancies evaluated by Rietveld refinement of XRD powder data exhibited perceptible deviation from linearity at the *p-n* transition. The increasing of minor sites occupancies and defects on boron sites seems to be vital for the overall enlargement of Zr content in the *β-rh* B structure. The coincidence of jump position in Seebeck coefficient *vs* Zr content dependencies (Fig. 7) with anomalies in atom site occupancies and lattice parameters within 1.88 at.% - 2.75 at.% Zr doping range (Fig. 3 and Fig. 4) suggest a possible correlation between these parameters in good agreement with the studies on Fe-doped *β-rh* B [21]. Current work leaves a room for further experiments (Raman- and IR-active phonons spectra measurements) to illuminate the changes in structural discontinuities. The electronic properties studies via electron structure calculations are in progress in order to understand the effects of metal concentrations on the control of *p–n* characteristics. From a practical point of view, the huge variation in the Seebeck coefficient values from positive to negative we find in Zr-doped *β-rh* B is quite striking. With the rare *n*-type behavior reaching values of -600 μVK^{-1}, it is significantly larger than the -200 μVK^{-1} observed in $YAlB_{14}$ with varying Al occupancy which has recently gained sizable attention [54-57].

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Figure Captions

Fig. 1. (a) Polyhedral view of the *β-rh* B structure showing B_{28} (orange) and B_{12} (yellow and white for icosahedra of type II and type I respectively) clusters and location of partially occupied Zr atom sites (Zr bonds are omitted). (b) Inter-linked B_{12} icosahedra (type II) along with Zr2, Zr77, B13 and B15. (c) Triply-fused type III icosahedra (B_{28} units) and B_{12} icosahedra (type I) along with Zr3, Zr11 and Zr44. (d) *D*-, (e) *E*-, (f) *F*-, (g) *N*- and (h) A_1-voids filled with Zr2, Zr3, Zr44, Zr11 and Zr77 respectively. In printed version, B - black balls, Zr - light-grey balls, B_{28} - dark grey units, isocahedra of type I and type II - white and light-grey units respectively.

Fig. 2. Powder XRD patterns of metal-poor (a) and metal-rich (b) Zr-doped *β-rh* B. The solid line derives from Rietveld refinement. $Y_{obs.}$-$Y_{calc.}$ is the intensity difference between experimental data and Rietveld calculations. Lowest raw of Bragg positions corresponds to the β-Si_3N_4 impurity originated from the mortar.

Fig. 3. Correlations between occupancies of *D*- and *E*-sites and Zr content in Zr-doped *β-rh* B.

Fig. 4. Zr concentration dependence of lattice constants and volume in Zr-doped *β-rh* B.

Fig. 5. Temperature dependence of resistivity of Zr-doped *β-rh* B samples. The compositions are given as obtained from Rietveld refinement of powder XRD data.

Fig. 6. Temperature dependence of thermopower of Zr-doped *β-rh* B samples. The compositions are given as obtained from Rietveld refinement of XRD data. Dashed lines are guidance to eye.

Fig. 7. Composition dependence of the Seebeck coefficient of Zr-doped *β-rh* B. Dashed lines are guidance to eye.