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Ternary Metal Borides [La,Ce,Pr,Nd,Sm] Os_4B_4 and [Y,La,Ce,Pr,Nd,Sm,Gd,Tb] Ir_4B_4 With $NdCo_4B_4$-Type Structure

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New ternary metal borides with composition $R. E. T_4B_4$ ($R. E.$ = rare earth metal, T = transition metal) have been synthesized within the systems [La,Ce,Pr,Nd,Sm]—Os—B and [Y, La, Ce, Pr, Nd, Sm, Gd, Tb]—Ir—B. All compounds were found to be crystallizing with $NdCo_4B_4$-type structure. Magnetic measurements (80-300 K, *Curie-Weiss* behaviour, $\theta_p \sim 16$ K and $\mu_{\text{eff}} = 9.94\, \mu_B$ for $TbIr_4B_4$) indicate Y and $R. E.$ elements (except Ce) to be trivalent in these compounds. The crystal chemistry of the isotypic series [Y, $R. E.$] $[Os,Ir]_4B_4$ is discussed.

(Keywords: Borides; Magnetic measurements; Rare earth systems; Structural chemistry; Ternary metal borides)

Ternäre Metallboride. [La,Ce,Pr,Nd,Sm]Os_4B_4 *und* [Y,La,Ce,Pr,Nd,Sm,Gd,Tb]Ir_4B_4 *mit* $NdCo_4B_4$-*Struktur*

Es wurden neue Metallboride der Zusammensetzung $R. E. T_4B_4$ ($R. E.$ = Seltenerdmetall, T = Übergangsmetall) innerhalb der Systeme [La,Ce, Pr,Nd,Sm]—Os—B und [Y,La,Ce,Pr,Nd,Sm,Gd,Tb]—Ir—B hergestellt. Alle Verbindungen kristallisieren entsprechend dem $NdCo_4B_4$-Typ. Magnetische Messungen (80—300 K, *Curie-Weiss*-Verhalten, $\theta_p \sim 16$ K und $\mu_{\text{eff}} = 9{,}94\, \mu_B$ für $TbIr_4B_4$) zeigen an, daß Y und die $R. E.$-Elemente (ausgenommen Ce) in diesen Verbindungen trivalent sind. Die Kristallchemie der isotypen [Y, $R. E.$][Os,Ir]$_4B_4$-Verbindungen wird diskutiert.

Introduction

$R. E.$—[Ru,Rh]—B systems have been partially studied by *Matthias* and coworkers and $R. E.$ [Ru,Rh]$_4B_4$-compounds with interesting magnetic and superconducting properties have been reported[4,5,6].

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Recent X-ray investigations of the boron-rich isothermal section of the systems [Y,Ln]—[Ru,Os]—B showed the existence of a series of isotypic compounds with $YCrB_4$-type structure[1,2]. Compound formation was found to be restricted to Y as well as the smaller rare earth atoms. Existence of new boride phases with an approximate boron content of ~50 at % was indicated from alloys containing larger rare earth atoms and osmium. Thus our attention was drawn to the monoboride region of the systems [Y,Ln]—[Os,Ir]—B. From recent phasediagram studies[7] within the systems [Sc,Zr,Hf]—[Rh,Ir]—B, compound formation was to be expected in the noble metal-boron rich region of the ternary systems (composition: $R.E.T_3B_4$ or $R.E.T_4B_4$).

Experimental

Sample preparation of ternary alloys: noble metal-rare earth-boron has recently been described in detail[1,2]. The temperature, used for final heat treatment was 1 400 °C for 8 h on a Boronitride substrate in a tungsten mesh high vacuum furnace. All compounds could be prepared single phase or nearly so. Os,Ir: powders, Degussa G.B. Hanau, BRD, 99.9 %; Y,La, *R.E.*: metal ingots: Ventron GmbH., Karlsruhe, BRD, m3N; B: crystall., Koch Light Lbs. Colnbrook, England 99 %.

Lattice parameters (and standard deviations) were evaluated by least squares fit extrapolation method from *Debye-Scherrer* photographs as well as from a *Siemens* powder diffractometer (filtered CrK_α, CuK_α). Atomic parameters and distances were refined from diffractometer intensity data [peak areas measured by polarplanimetry, intensity least squares program ILS[3]].

Susceptibility measurements were performed with a pendulum susceptibility meter (Faraday compensation method) within the temperature range 80-300 K. Experimental details see Ref.[1,2]. (Susceptibility measuring device, Sus-10, Anton Paar KG., Graz, Austria.)

Results and Discussion

X-ray powder diffraction inspection of Y—Ir—B alloys with nominal composition in at %: Y(12)Ir(36)B(52) [in search for $ZrIr_3B_4$-type compounds like $ScIr_3B_4$, see Ref.[7]] revealed the existence of a new ternary compound. Homogeneous samples were obtained after heat treatment for 24 h at 1 400 °C at a composition of Y(11)Ir(44)B(45).

The powder pattern of the new phase resembled those found earlier in some *R.E.*—[Os,Ir]—B alloys prepared for a composition 1:1:4 in search for $YCrB_4$-type phases[1]. Thus according to the generally similar alloying behaviour of Y and the rare earth-metals, compound formation was investigated for all combinations [Y,La, *R.E.*]—[Os,Ir]—B. The compositions studied were 1:3:4 as well as 1:4:4.

Compound formation at composition 1:4:4 indeed was observed within all the systems: [Y,La,Ce,Pr,Nd,Sm,Gd,Tb,Dy,Ho,Er,Tm, Yb]—Os—B as well as [La,Ce,Pr,Nd,Sm,Gd,Tb]—Ir—B.

No attempts were made to synthesize analogous samples containing Pm, Eu, and Lu. The powder patterns of single phase [La,Ce,Pr, Nd,Sm,Gd,Tb]—Ir—B as well as [La,Ce,Pr,Nd,Sm]—Os—B alloys compare well with the one obtained for Y(11)Ir(44)B(45). Similar but slightly different powder diagrams were obtained for [Y,Gd, Tb,Dy,Ho,Er,Tm,Yb]—Os—B alloys indicating a different but isotypic series[12].

In case of [Y,Gd,Tb]—Ir—B alloys the typical powder pattern of the new phase is not directly obtained from arc melted samples, but only after prolonged heat treatment at 1 400 °C (24 h). Faint reflexions of the new phase have been also observed in Dy—Ir—B alloys, however no singlephase samples could be obtained so far (even for long time heat treatment 64 h, 1 200 °C) indicating very low stability or metastability of this compound. Furthermore [Ho,Er,Tm,Yb]—Ir—B samples proved to be multiphase with different and more complicated powder patterns.

Table 1. *Lattice parameters and volume of the new ternary borides:* [Y, *R. E.*][Os,Ir]$_4$B$_4$ (NdCo$_4$B$_4$-*type structure*)

Phase	a ± 0.003 Å	c ± 0.002 Å	c/a	V (Å^3)
$LaOs_4B_4$	7.611	3.998	0.525	231.6
$CeOs_4B_4$	7.538	4.005	0.532	227.5
$PrOs_4B_4$	7.567	4.002	0.529	229.2
$NdOs_4B_4$	7.552	4.003	0.530	228.3
$SmOs_4B_4$	7.526	4.009	0.533	227.1
YIr_4B_4	7.547	3.980	0.527	226.7
$LaIr_4B_4$	7.662	3.972	0.518	233.1
$CeIr_4B_4$	7.642	3.970	0.520	231.8
$PrIr_4B_4$	7.629	3.974	0.521	231.3
$NdIr_4B_4$	7.616	3.974	0.522	230.5
$SmIr_4B_4$	7.590	3.976	0.524	229.0
$GdIr_4B_4$	7.571	3.979	0.526	228.1
$TbIr_4B_4$	7.557	3.979	0.527	227.2

Well crystallized samples of the new phase are easily obtained from arc melted La—Os—B alloys. A single crystal was found by mechanical fragmentation of a melted sample $La_{0.11}Os_{0.44}B_{0.45}$.

Table 2. *Powder diffraction data for* $NdIr_4B_4$ ($NdCo_4B_4$ *type*)

Material: Alloy $Nd_{.11}Ir_{.44}B_{.45}$, arc melted.

Method: Powder X-ray diffraction in a Siemens Diffractometer, Ni-filtered CuK_α-radiation, Si-standard, $I = mF^2\,(1 + \cos^2 2\theta / \sin^2\theta \cdot \cos\theta)$ is normalized to the strongest reflexion having intensity 100. Anomalous dispersion correction after *Cromer* and *Libermann*. $\Sigma|\Delta I| / \Sigma I_0 = 0.10$.

Space Group: C^4_{4h}—$P4_2/n$, No. 86, origin at $\bar{1}$.

2 Nd in 2*b*) 1/4, 1/4, 3/4;		$B = 0.4\,Å^2$
8 Ir in 8*g*) x, y, z;	$x = 0.598\,(3), y = 0.138\,(2), z = 0.144\,(2)$:	$B = 0.5\,Å^2$
8 B in 8*g*) x, y, z;	$x = 0.533, y = 0.410, z = 0.137$:	$B = 0.9\,Å^2$

	$10^4 \cdot \sin^2\theta$		Intensity	
hkl	obs.	calc.	obs.	calc.
110	204	205	**	20.2
200	*	409	*	0.8
101	479	478	3	3.6
111	579	580	25	33.1
201	784	785	4	3.1
220	818	818	2	1.7
211	885	887	100	94.9
121				5.1
310	1021	1023	63	11.4
130				47.2
221	1193	1194	33	25.7
301	*	1296	*	0.0
311	1395	1399	14	11.8
131				1.3
002	1498	1503	3	2.6
102	1606	1605	39	22.2
400	1636	1637		11.1
321	1706	1705	19	6.8
231				10.5
112		1707		0.3
330	1838	1841	2	2.2
202	1910	1912	1	1.0
401	*	2012	*	0.2
212		2014	12	0.0
122				1.0
420	2045	2046		9.0
240				0.5
411	2115	2115	3	0.8
141				1.7
331	*	2217	*	0.6
222	*	2321	*	0.8
421	2421	2421	19	0.1
241				1.3
302		2423		13.5

Tabelle 2 (Fortsetzung)

	$10^4 \cdot \sin^2\theta$		Intensity	
hkl	obs.	calc.	obs.	calc.
312	2526	2526	4	1.4
132				3.0
510	2658	2659	5	0.5
150				3.9
322	2831	2832	3	1.4
232				0.9
431	2931	2933	17	0.8
341				5.7
501				5.7
511	3035	3035	5	3.5
151				0.2
402	*	3139	*	0.0
412	3239	3242	20	0.8
142				10.7
440	3271	3273		5.6
521	3340	3342	9	4.5
251				2.8
332		3344		0.0
530	3478	3478	3	2.2
350				0.1
103		3483		0.6
422	3584	3548	5	1.1
242				0.7
113		3586		2.4
441		3649		0.1
600		3682		0.8
203	*	3790	*	0.5
531	3849	3853	6	0.0
351				3.6
213	3893	3893		0.3
123				1.5
601	4058	4058	15	1.5
432		4060		7.7
342				1.1
502				1.4
620		4091		0.2
260				0.9
611	4159	4160	11	3.1
161				0.5
512		4162		0.3
152				0.6
223	4197	4199		6.0

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* Not observed.

** Not used in refinement.

Weissenberg photographs (needle axis [001]) proved the crystal to be tetragonal with low *Laue* Symmetry ($4/m$). Powder patterns of all compounds could be indexed completely on the basis of this tetragonal cell (Table 1), confirming the extinctions ($hk0$) for $h + k = 2n + 1$ and in addition ($00l$) for $l = 2n + 1$. Thus the only possible space group is $P4_2/n$. Small changes in the lattice parameters with composition were observed from multiphase alloys, indicating only a narrow homogeneity region (1 400 °C). Thus a formula $R.E.(\mathrm{Os,Ir})_4\mathrm{B}_4$ is representative. Comparison of the atomic volumes with the volume of the unit cell—assuming a space filling of $\sim 70\%$—indicates two formula units of $R.E.\,[\mathrm{Os,Ir}]_4\mathrm{B}_4$. Composition, lattice parameters, observed extinctions as well as intensities reveal structural identity with the recently described crystall structure of $\mathrm{NdCo_4B_4}$ (Ref.[8]). From Table 1a slightly different c/a-ratio was found to be characteristic for the two series of compounds $R.E.\mathrm{Os_4B_4}$ and $R.E.\mathrm{Ir_4B_4}$. Furthermore small but characteristic intensity differences owing to different T-atom parameters were observed from powder diagrams of iridium and osmium compounds respectively. For the osmium-series atomic parameters could be derived from intensity analysis of powder diagrams as well as zeroth and first layer level *Weissenberg* photographs of $\mathrm{LaOs_4B_4}$, CuK_α, $x_{\mathrm{Os}} = 0.605(3)$, $y_{\mathrm{Os}} = 0.140(3)$, $z_{\mathrm{Os}} = 0.140(3)$]. In case of the iridium series $R.E.\,\mathrm{Ir_4B_4}$, precise atomic parameters (and distances) were evaluated for $\mathrm{NdIr_4B_4}$ from a least squares refinement of powder diffractometer intensity data, yielding a reliability factor of $R = 10\%$ (see Tables 2, 3). The atomic parameters for $R.E.\,\mathrm{Os_4B_4}$ as well as $R.E.\,\mathrm{Ir_4B_4}$ are only

Table 3. *Interatomic distances* (< 4 Å) *in* $\mathrm{NdIr_4B_4}$

Nd—2 Nd	3.979	B—1 Nd	2.919
—4 Ir	3.198	—1 Nd	3.107
—4 Ir	3.206	—1 Ir	2.118
—4 B	2.919	—1 Ir	2.173
—4 B	3.107	—1 Ir	2.135
		—1 Ir	2.124
Ir—1 Nd	3.206	—1 B	1.819
—1 Nd	3.198		
—4 Ir	2.847		
—1 Ir	2.880		
—1 Ir	2.825		
—1 B	2.173		
—1 B	2.124		
—1 B	2.135		
—1 B	2.118		

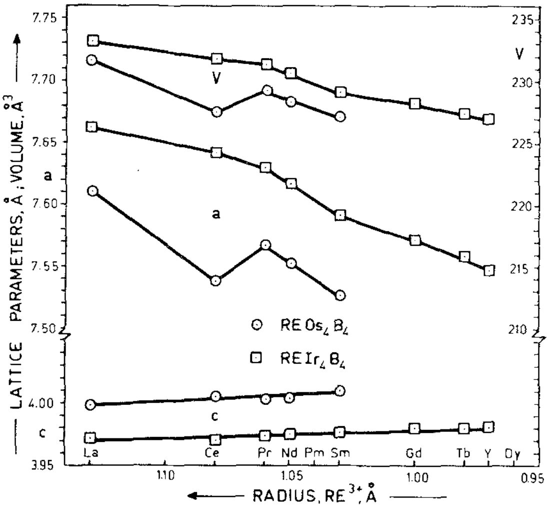

Fig. 1. Lattice parameters and volumes of the new ternary borides $[Y, R.E.][Os,Ir]_4B_4$ versus $R_{R.E.}{}^{3+}$

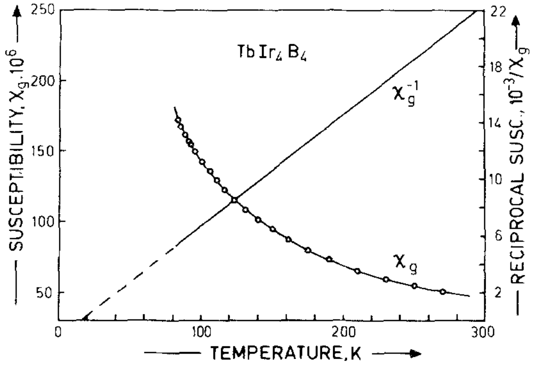

Fig. 2. Gram- and reciprocal gram-susceptibility versus temperature for $TbIr_4B_4$

slightly different from those derived for $NdCo_4B_4$ (Ref.[8]). Using these two sets of atomic parameters, observed and calculated powder intensities for all $R.E.[Os,Ir]_4B_4$ compounds are in excellent agreement. Calculations can be obtained on request.

Lattice parameters and volumes show linear dependency from $R.E.^{3+}$ radius (see Fig. 1; radii were taken from *Dickinson*[9] except La = 1.13 Å and Y = 0.97 Å; see also Ref.[10]). Furthermore lattice parameters and volume of the Y compound range between the values for Tb and Dy, thus indicating the *R.E.* atoms as well as Y to be in a trivalent state. The lower lattice parameters (and volumes) for the cerium-compounds reflect the generally ambivalent ($3^+/4^+$) behavious of cerium.

Magnetic measurements were performed on a single phase alloy of $TbIr_4B_4$. Linear temperature dependency of the reciprocal gram susceptibility χ_g^{-1} (emu/g) displays *Curie-Weiss* behaviour within the temperature region investigated (80-300 K; $\theta_p \approx 16$ K). The paramagnetic moment per formula unit was calculated from the *Curie-Weiss* constant $\mu_{\text{eff}} = 2.84 \sqrt{C_M}$ to be $9.94\,\mu_B$ in very close agreement with the theoretical value $g\sqrt{J(J+1)}\,\mu_B = 9.72\,\mu_B$ for Tb^{3+}(Fig. 2).

The linear correlation: lattice parameters versus $R_{R.E.^{3+}}$ as well as the magnetic behaviour indicates the (Ln,Y) elements to be in a trivalent state in *R.E.* $(Os,Ir)_4B_4$ type phases.

Bonding in borides with higher metal content ($M/B > 1$) is still far from being well understood. Thus the nature of the trivalent behaviour of *R.E.* elements in binary as well as ternary borides has not to be misinterpreted in terms of i.e. a $R.E.^{3+}$ halide. This can simply be seen from the fact, that from volume considerations the $R.E.^{3+}$ atom volumes in i.e. *R.E.* T_4B_4 compounds still are close to a normal *R.E.*-metal radius.

According to the classification scheme of ternary borides, recently presented[11], the metal/boron ratio > 1 is typical for the occurrence of isolated boron pairs or chain fragments. A characteristic difference between the three structure types of formula *R.E.* T_4B_4: (1) $CeCo_4B_4$; (2) $LuRu_4B_4$ and (3) $NdCo_4B_4$ can be found in the various mode of linking the VIII-A metal tetrahedra. In $CeCo_4B_4$ as well as $LuRu_4B_4$ sheets of tetrahedra are formed with isolated *R.E.*-atoms (in T_{VIII}metal cages) connecting the sheets. In $NdCo_4B_4$ the threedimensionally linked VIII-A metal frame work forms octogonal tubes giving space to infinite linear *R.E.*—*R.E.*-chains. Thus the better space filling concept for smaller rare earth atoms favors the $LuRu_4B_4$ and $CeCo_4B_4$ type structures. Indeed a coursery inspection of a single crystal fragment of "$Y_{\sim 1.25}Os_4B_4$" (Ref.[12]) revealed a new ternary structure type, closely related to the crystal structure of $NdCo_4B_4$, which can be understood as an adaption of the crystal structure of $NdCo_4B_4$ towards a higher ratio $R_{R.E.}/R_T$.

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