



# Valence-Electron-Driven Ru/Ti Site Preference in the New Ternary Boride $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Synthesis and Single-Crystal Structure Refinement

Boniface P. T. Fokwa

## ► To cite this version:

Boniface P. T. Fokwa. Valence-Electron-Driven Ru/Ti Site Preference in the New Ternary Boride  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Synthesis and Single-Crystal Structure Refinement. *Journal of Inorganic and General Chemistry / Zeitschrift für anorganische und allgemeine Chemie*, 2009, 635 (13-14), pp.2258. <10.1002/zaac.200900192>. <hal-00509229>

**HAL Id: hal-00509229**

**<https://hal.science/hal-00509229v1>**

Submitted on 11 Aug 2010

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

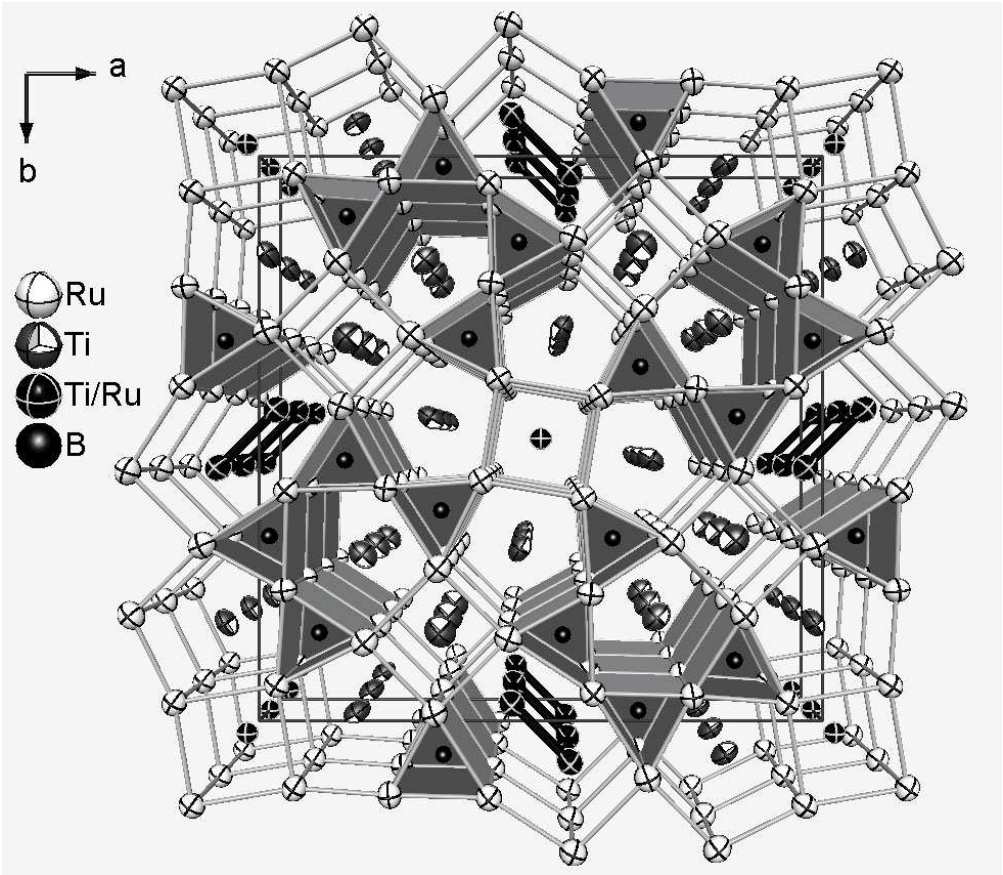


Zeitschrift für Anorganische und  
Allgemeine Chemie

**Valence-Electron-Driven Ru/Ti Site Preference in the New  
Ternary Boride Ti<sub>10</sub>Ru<sub>19</sub>B<sub>8</sub>: Synthesis and Single-Crystal  
Structure Refinement**

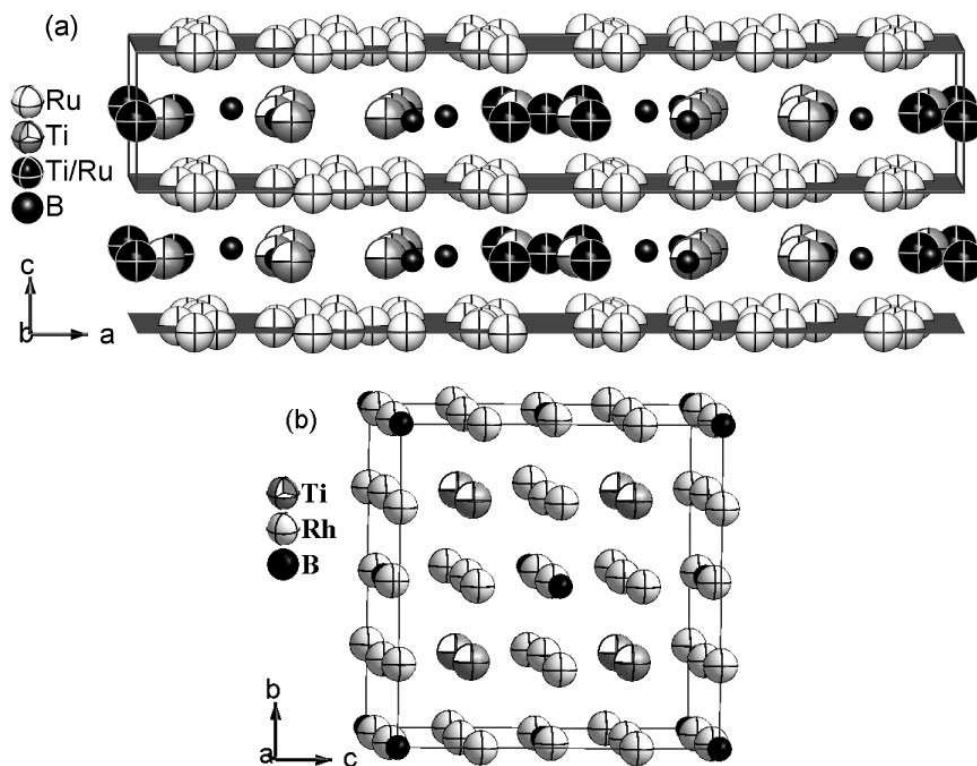
Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
Manuscript ID:	zaac.200900192.R1
Wiley - Manuscript type:	Article
Date Submitted by the Author:	04-Jun-2009
Complete List of Authors:	Fokwa, Boniface P. T.
Keywords:	Transition-metal borides, Zn <sub>11</sub> Rh <sub>18</sub> B <sub>8</sub> -type, Ti <sub>10</sub> Ru <sub>19</sub> B <sub>8</sub> , crystal structure, valence electrons





Perspective view along  $[001]$  of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ . Boron centered trigonal prisms and  $(\text{Ti/Ru})_2$ -dumbbells (black bonds) are highlighted. The ellipsoids are drawn at 99.9% probability level.

258x225mm (96 x 96 DPI)



(a) Projection nearly along  $[010]$  of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Ruthenium planes perpendicular to  $[001]$  are highlighted. (b) Projection nearly along  $[100]$  of the crystal structure of  $\text{Ti}_2\text{Rh}_6\text{B}$ : All planes are observed in three directions.

233x185mm (96 x 96 DPI)

## Full Paper

DOI: 10.1002/zaac.200((please insert the last 6 DOI digits))

# Valence-Electron-Driven Ru/Ti Site Preference in the New Ternary Boride $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Synthesis and Single-Crystal Structure Refinement

**Boniface P. T. Fokwa\***

Institute of Inorganic Chemistry, RWTH Aachen University, D-52056 Aachen, Germany

**\* Dr. Boniface P. T. Fokwa**

Institute of Inorganic Chemistry, RWTH Aachen University

D-52056 Aachen

Fax: (+)49 2418092642

E-mail: boniface.fokwa@ac.rwth-aachen.de

Received ((will be filled in by the editorial staff))

**Abstract.** Powder samples and single crystals of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  were synthesized by arc-melting the elements in a water-cooled copper crucible under an argon atmosphere and characterized by single-crystal X-Ray diffraction and energy-dispersive X-ray analysis. The new silver-like compound crystallizes in the tetragonal system with the  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type structure (space group  $P4/mbm$  (no. 127),  $Z = 2$ ;  $a = 17.591(5) \text{ \AA}$ ,  $c = 2.9645(13) \text{ \AA}$ ,  $R_1 = 0.0708$ ,  $wR_2 = 0.0992$ ,  $GooF = 1.047$  for all 1266 reflections and 58 parameters). The interesting characteristic in this new ternary variant is the valence electron driven site-preferential mixture of both titanium and ruthenium forming “ladders” along the [001] direction.

**Keywords:** Transition-metal borides,  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ , crystal structure,  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type, valence electrons

## Introduction

Recently we reported the first ferromagnetic transition metal boride containing ladders of a magnetically active element (iron),  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  [1]. Other quaternary derivatives of the  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type structure,  $\text{Zn}_{10}\text{MRh}_{18}\text{B}_8$  ( $M = \text{Cr, Mn, Fe, Co, Ni}$ ) [2] have also been reported but they contain the well documented one dimensional chains of a magnetically active element  $M$  [3-7]. In fact substituting either zinc in  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ , or titanium in a hypothetical “ $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ” by iron, leads to the different local structures observed. In the

ternaries  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  and hypothetical " $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ " both zinc and titanium atoms occupy tetragonal, pentagonal and elongated hexagonal prisms of rhodium or ruthenium atoms, respectively, with the elongated hexagonal prisms accommodating two atoms (as "dumbbells"). In terms of volume, one-half of the elongated hexagonal prism, i.e. the volume accommodating only one atom of the dumbbell, is smaller than a single pentagonal prism, but larger than a tetragonal prism. Consequently, if atomic size factors are influential for the stability of these compounds, substituting zinc and titanium by iron, respectively, in  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  and " $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ " should give the same result, since both zinc (atomic radius,  $r_a = 1.31 \text{ \AA}$ ) and titanium ( $r_a = 1.38 \text{ \AA}$ ) are clearly larger than iron ( $r_a = 1.25 \text{ \AA}$ ). However, different substitution patterns emerge:  $\text{Zn}_{10}\text{FeRh}_{18}\text{B}_8$  finds iron replacing zinc atoms in the smallest tetragonal prism, as expected from size considerations; whereas in  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ , iron has replaced titanium preferentially and unexpectedly in the elongated hexagonal prisms. Therefore, electronic factors should play a key role in understanding the substitution preference of titanium by iron in hypothetical " $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ", leading to  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  [1]. The present work deals with the synthesis and structural characterization of the hypothetical " $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ". A successful synthesis should lead not only to the first phase in the Ti–Ru–B system, but also to a better understanding of the substitution preference mentioned above.

## Experimental Section

### *Synthesis*

The title compound was synthesized by arc-melting the elements in a water-cooled copper crucible under an argon atmosphere using a tungsten tip as a second electrode. The starting elements, titanium (pieces, 99.9 %, Degussa), ruthenium (powder, 99.9%, Umicore) and boron (pieces, 99.999%, Alfa Aesar) were weighed in the atomic ratio 11:18:8 according to the hypothetical formula " $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ". In another synthesis ruthenium was used in excess (50% more, ratio 11:27:8). The well homogenized educts were pressed into pellets and arc-melted under argon. The argon was purified over silica gel, molecular sieves, and titanium sponge (950 K). Weight losses during the melting process were negligible. A silver-like product with metallic luster containing some single crystals (only in the second synthesis) suitable for X-ray structure analysis was obtained. These needle-shaped crystals could easily be isolated manually under an optical microscope for X-ray single-crystal analysis. Powder diffractograms of the silver-like products were taken using a Guinier powder diffractometer with  $\text{Cu-K}\alpha_1$  radiation ( $\lambda = 1.54059 \text{ \AA}$ ) and silicon as an internal standard. Phase analyses and

lattice parameter refinements were carried out using the program WINXPOW [8]. The presence of the two metals and their ratio were characterized by Energy Dispersive X-ray analysis (EDX) on a high-resolution, low-energy SEM of the type LEO 1530 (Oberkochen, Germany) equipped with an EDX system of the type INCA (Oxford, England). EDX measurements on several selected crystals provided the ratio 1:1.92 (Ti:Ru) (averaged experimental data) for crystals obtained from the second synthesis.

### ***Crystal Structure Determination***

Two single crystals of suitable sizes were fixed in glass capillaries and data were collected on a CCD single crystal diffractometer (Bruker SMART APEX) with graphite-monochromatized Mo- $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The X-ray intensities were corrected for absorption using a semi-empirical procedure [9]. The crystal structure was refined by full-matrix least squares refinement [10], based on  $F^2$ , using anisotropic displacement parameters for all metals (Ti, Ru) and isotropic ones for B. The initial structure file of  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  (starting model) was first transformed to the standard setting using the program SETSTRU from the Bilbao Crystallographic Server [11]. All relevant crystallographic data and experimental details of the data collection are listed in Table 1. Table 2 contains the atomic coordinates and displacement parameters, while Table 3 summarizes selected interatomic distances. Crystal structure drawings were produced using the program *Diamond* [12]. A listing of all refinement data and data collection is available <sup>1)</sup>.

1): More details on the structure determination may be obtained from the Fachinformationszentrum Karlsruhe (e-mail address: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de)), D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the CSD depository number: CSD 420561

## **Results and Discussion**

### ***Phase analysis***

From phase analyses of the powder data, the expected  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type phase could easily be identified either for 11:18:8 (Ti:Ru:B) or for 11:27:8 starting compositions. In the first case the expected phase was only the second component (about 30% yield), as cubic TiRu [13] was found to be the main phase. Because this synthesis was not successful as hoped, we started a second synthesis using ruthenium in excess because from size and electronic (Valence electrons, VE) considerations ruthenium is nearer to iron than titanium (note that the starting point for this work was  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  where iron was substituted by titanium). As a

consequence, the yield of the expected phase could be increased to about 80%, with hexagonal  $\text{Ti}_{0.1}\text{Ru}_{0.9}$  [13] identified as the second phase. The presence of ruthenium in the second phase could be expected (used in excess) but not titanium. Although only in small amount the presence of titanium in the second phase ( $\text{Ti}_{0.1}\text{Ru}_{0.9}$ ) indicates that we may expect less titanium in the main phase. In both syntheses some small unidentified intensities were present in the powder diffractograms. Nevertheless the lattice parameters [ $(a = 17.557(5) \text{ \AA}$ ,  $c = 2.9731(8) \text{ \AA}$ ,  $V = 916.4(6) \text{ \AA}^3$ ) and  $(a = 17.560(5) \text{ \AA}$ ,  $c = 2.9603(8) \text{ \AA}$ ,  $V = 912.8(6) \text{ \AA}^3$ )] could be refined, respectively for the first and second synthesis. The volume difference is  $3.6 \text{ \AA}^3$  indicating a higher titanium/ruthenium ratio in the product from the first synthesis than from the second, and therefore a phase width. However this homogeneity range can only be studied using single crystals because of the presence of side products in the powder samples. Single crystals were found only in the second experiment and, given the excess of ruthenium used, it is expected that the maximum amount of ruthenium that may enter the structure will be determined. From the crystals obtained, two were suitable for single-crystal structure analysis.

### Structure refinement

The standardized  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  structure was used as starting model for the single-crystal structure refinements, but replacing iron by titanium, thus the starting composition was “ $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ”. After a few refinement cycles, the structure type was confirmed but the refinement did not converge. In fact, in the difference Fourier map a high peak ( $21.05 \text{ e/\AA}^3$ ) was found at only  $0.04 \text{ \AA}$  far from the fifth titanium site (Ti5,  $4h$ , i.e. the iron site in  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ ). Furthermore, the displacement parameters of Ti5 were meaningless (too small compared to the other titanium sites and non positive definite). All these discrepancies suggested that this site needs more electrons. However a refinement using the electron richer ruthenium alone at the Ti5 site also leads to bad results (with very large displacement parameters). Good results were then achieved after refining with both ruthenium and titanium at the Ti5 position (mixed occupancy refinement), and this leads to the highest and lowest peaks in the difference Fourier map of only  $3.25 \text{ e/\AA}^3$  and  $-2.41 \text{ e/\AA}^3$  respectively. The refinements did converge at this point (for both single crystals) but the displacement parameters of one titanium atom (Ti2, site  $2b$ ) were not fully satisfactory as they were a bit smaller than those of the other titanium atoms. A mixed occupancy refinement was therefore used also for this site: Although the  $R$ -values did not change at this point, the displacement parameters for the  $2b$  site improved significantly. In the final proper refinement ( $R_1 = 0.071$ ,



$wR_2 = 0.099$  for all 1269 reflections, 58 parameters and no restraint) the overall occupancies for Ti5/Ru6 and Ti2/Ru7 sites were constrained to unity and the individual occupancies were refined to 0.538(13)/0.462(13) for Ti5/Ru6 and 0.970(16)/0.030(16) for Ti2/Ru7, leading to the formula  $\text{Ti}_{10.05(4)}\text{Ru}_{18.95(4)}\text{B}_8$ . Nearly the same composition was obtained from the second single crystal ( $\text{Ti}_{10.03(4)}\text{Ru}_{18.97(4)}\text{B}_8$ ) as expected from phase analysis. Therefore the formula  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  may be retained within experimental error for this phase and will be used in the following. These results were in full agreement with EDX analyses on several crystals (see experimental part), inducing that a maximum of 19 ruthenium atoms may enter the structure. Nevertheless another study will be needed to identifying the phase width  $x$  of  $\text{Ti}_{11-x}\text{Ru}_{18+x}\text{B}_8$ : Precisely, to determine the maximal amount of titanium that may enter this structure.

-----Figure 1-----

### **Structural chemistry**

$\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  crystallizes, like  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ ,  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  and  $\text{Zn}_{10}\text{MRh}_{18}\text{B}_8$  ( $M = \text{Sc} - \text{Cu}, \text{Al}, \text{Si}, \text{Ge}, \text{Sn}$ ), in the tetragonal system in space group  $P4/mbm$ . Its crystal structure deviates from  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  structure mainly because the  $\text{Fe}_2$ -ladder subunit is replaced by the  $(\text{Ti5/Ru6})_2$ -ladder, thus reducing the number of valence electrons (VE) from 220 ( $4 \times 9 + 8 \times 2 + 8 \times 18 + 3 \times 8 = 220$ ) for  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  to 216 for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ . The hypothetical and originally targeted “ $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ” composition has 212 VE i.e. 4 VE less than the synthesized  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ , suggesting that the iron position in  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  structure may not be fully substituted by elements with a number of VE smaller than that of iron by at least four electrons (e.g. Ti, Sc, ...). In other words the number of VE of titanium is not sufficient to fulfill the requirements (bonding to itself and to the neighboring atoms) needed for this site. From a theoretical point of view it was deduced, via the pseudogap observed in the calculated density of states of  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ , that its structure could accommodate even more valence electrons (up to 13 VE) [1]. This deduction may open the way for the synthesis of electron richer compounds crystallizing with the same structure type (this study is being done). Then again, the theory does not give the VE number at which the structure will collapse if we remove some electrons, thereby destabilizing this structure type. The actual result ( $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ , 216 VE) suggests that four VE may be removed from  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  (220 VE) without destroying the structure. Attempts to decrease even more the number of VE by replacing titanium with scandium are underway.

By comparing  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  with  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  it becomes clear why different substitution patterns occur en route to the quaternaries  $\text{Zn}_{10}\text{FeRh}_{18}\text{B}_8$  and  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ . In the two ternary phases zinc and titanium are present at the same sites with the exception of the  $4h$  site where  $\text{Zn}_2$ - and  $(\text{Ti}_5/\text{Ru}_6)_2$ -dumbbells are found: In fact all tetragonal and pentagonal prisms present in  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  and  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  (built up by rhodium and ruthenium, respectively) are centered respectively by zinc or titanium, although both prisms are the smallest and the largest available for the two elements (see figure 1). The middle-sized prism (elongated hexagonal prism) is also centered as expected by zinc in  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  but not by titanium alone in  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ . From size considerations one would also expect titanium alone at this  $4h$  site, since both zinc (atomic radius,  $r_a = 1.31 \text{ \AA}$ ) and titanium ( $r_a = 1.38 \text{ \AA}$ ) are clearly larger than iron ( $r_a = 1.25 \text{ \AA}$ ) [14]. The fact that titanium can only fill the  $4h$  site together with the electron richer but smaller ruthenium is the proof, that this site needs more valence electrons than the four available for titanium. Therefore, the syntheses of the stoichiometric quaternary derivatives “ $\text{Ti}_9\text{M}_2\text{Ru}_{18}\text{B}_8$ ” ( $\text{M} = \text{Cr} - \text{Zn}$ ) should be possible because at this  $4h$  site more valence electrons will be available from the M-elements compared to titanium. On the contrary, the synthesis of stoichiometric “ $\text{Ti}_9\text{Sc}_2\text{Ru}_{18}\text{B}_8$ ” should not be possible. The VE driven site preference observed in the Ti-based phases, particularly for the  $4h$  site, is the main difference if compared with the Zn-based phases of the  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$  structure type. It is also the main reason why stoichiometric “ $\text{Ti}_{11}\text{Ru}_{18}\text{B}_8$ ” is not accessible experimentally. Attempts to synthesize the  $\text{Zn}_{10}\text{FeRh}_{18}\text{B}_8$ -related “ $\text{Ti}_{10}\text{FeRu}_{18}\text{B}_8$ ” also failed, as expected.

The COHP analysis performed for  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ , suggested, that it is the heteroatomic Ru–B and Ru–Ti bonds that create its structural stability [1]. The new ternary isotype  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  is expected to be also stabilized by these two bonds, because the distances observed in both phases are quite similar, even the distance in the  $\text{Fe}_2$ -dumbbell ( $2.49 \text{ \AA}$ ) is nearly the same as that of the unexpected  $(\text{Ti}_5/\text{Ru}_6)_2$ -dumbbell ( $2.46 \text{ \AA}$ ).

The relatively short Ru–B distances, ranging from  $2.16 \text{ \AA}$  to  $2.22 \text{ \AA}$  (average,  $2.19 \text{ \AA}$ , see table 3) are only slightly longer than the sum of their covalent radii ( $2.07 \text{ \AA}$ ), suggesting very strong bonding interactions. Similar Ru–B interatomic distances are found in the phases  $\text{Ru}_2\text{B}_3$  (average,  $2.18 \text{ \AA}$ ) [15],  $\text{Fe}_x\text{Ru}_{7-x}\text{B}_3$  ( $0 < x \leq 1.5$ ; average,  $2.14 \text{ \AA}$ ) [16],  $\text{Ti}_{1.6}\text{Os}_{1.4}\text{RuB}_2$  ( $2.16 \text{ \AA}$ ) [17] and of course  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$  (average,  $2.18 \text{ \AA}$ ). As said before, strong bonding is also expected for the Ti–Ru interaction, and this is reflected in the average distance ( $2.71 \text{ \AA}$ ) being nearly the same as the sum of their metallic radii for CN 8 (ca.  $2.72 \text{ \AA}$ ) [14]. The average Ru–M ( $\text{M} = \text{Ti}_5/\text{Ru}_6$ ) distance of  $2.75 \text{ \AA}$  lies, as could be expected, between the sum of the metallic radii for CN 12 for Ru–Ti ( $2.80 \text{ \AA}$ ) and Ru–Ru ( $2.67 \text{ \AA}$ ) [14]. As a

consequence of these significant heteroatomic interactions between Ru atoms and the other elements, homoatomic Ru–Ru interactions are expected to be weaker than in elemental Ru, because greater electron densities are engaged in Ru–X (X = B, Ti, Ti/Ru) bonds. As expected a wide range of Ru–Ru distances is observed in  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ , with an average of 2.85 Å that is significantly longer than the ruthenium metallic distance for CN12 (2.67 Å) [14]. The (Ti/Ru)<sub>2</sub>-dumbbell has a rather short distance, 2.46 Å, which is shorter than the sum of the metallic radii for CN 12 for Ru–Ru (2.67 Å) and Ti–Ti (2.93 Å). Therefore strong bonding is expected as observed for Fe<sub>2</sub>-dumbbell (2.49 Å) in  $\text{Ti}_9\text{Fe}_2\text{Ru}_{18}\text{B}_8$ .

No significant interactions were found for Ti–(Ti/Ru) and Ti–B contacts in the structure.

-----Figure 2-----

### ***Comparison with other ternary transition-metal-rich borides containing at least one of the two metals***

$\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  is the first compound in the Ti–Ru–B system. In fact, only fourteen ternary transition-metal-rich borides are known so far, which contain at least one of the two metals: From these fourteen, four borides contain titanium and ten contain ruthenium. They can be divided in two groups:

a) In the first group a preferred orientation is observed in their crystal structures: A layer-like arrangement of all atoms into two different sheets perpendicular to only one direction.  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  meets exactly this requirement (see figure 2a), and is therefore structurally related to  $\text{Ti}_3\text{Co}_5\text{B}_2$ ,  $\text{Ti}_2\text{ReB}_2$  ( $\text{U}_3\text{Si}_2$  type),  $\text{YRu}_3\text{B}_2$  ( $\text{CeCo}_3\text{B}_2$ -type), and  $\text{Sc}_2\text{Ru}_5\text{B}_4$  [18]. In all these cases the most represented metal builds one layer, which connects to the identical adjacent one, thereby building prisms in which the other metal and boron are located (see for example figure 1).

b) A three dimensional arrangement of all atoms without any preferred orientation forms the second group. The ten remaining ternary transition-metal-rich borides (from the fourteen mentioned above) fulfil this requirement (see for example figure 2b): The double perovskite-like  $\text{Ti}_2\text{Rh}_6\text{B}$  [19], the  $\tau$ -borides ( $\text{Ti}_2\text{M}_{21}\text{B}_6$ ,  $\text{Ti}_3\text{M}_{20}\text{B}_6$  M = Co, Ni; and  $\text{Ta}_{3.25}\text{Ru}_{19.75}\text{B}_6$ , all  $\text{Cr}_{23}\text{C}_6$ -type) [18], the  $\text{Th}_7\text{Fe}_3$ -type  $\text{Fe}_x\text{Ru}_{7-x}\text{B}_3$  [16],  $\text{W}_{1.75}\text{Ru}_{1.25}\text{B}_2$  ( $\text{Mo}_2\text{IrB}_2$ -type), and  $\text{MRu}_4\text{B}_4$  (M = Y, Sc) [18] did not show any preferred orientation and are therefore structurally not related to  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ .

## Conclusion

The new phase  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  was successfully synthesized (as polycrystalline sample and single crystals) from the elements and characterized by X-ray single-crystal analysis and EDX measurements. It is the first ternary compound in the Ti-Ru-B system.  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$  crystallizes as a substitutional variant of the  $\text{Zn}_{11}\text{Rh}_{18}\text{B}_8$ -type structure, and a valence electron driven site preference is observed for the Ru/Ti mixture.

## Acknowledgments

I thank my mentor, Prof. Dr. Richard Dronskowski, for the great support during my habilitation in his group. The Deutsche Forschungsgemeinschaft is gratefully acknowledged for financial support, Dr. Roland Winde (Umicore, Hanau-Wolfgang) for the kind donation of ruthenium metal, Resi Zaunbrecher (IPC, RWTH-Aachen) for the EDX analysis and Christian Goerens for experimental help.

## References

- [1] B. P. T. Fokwa, G. D. Samolyuk, G. J. Miller, R. Dronskowski, *Inorg. Chem.* **2008**, *47*, 2113.
- [2] U. Eibenstein, W. Jung, *Z. Anorg. Allg. Chem.* **1998**, *624*, 802-806.
- [3] E. A. Nagelschmitz, W. Jung, *Chem. Mater.* **1998**, *10*, 3189.
- [4] E. A. Nagelschmitz, W. Jung, R. Feiten, P. Müller, H. Lueken, *Z. Anorg. Allg. Chem.* **2001**, *627*, 523.
- [5] R. Dronskowski, K. Korczak, H. Lueken, W. Jung, *Angew. Chem.* **2002**, *114*, 2638; *Angew. Chem. Int. Ed.* **2002**, *41*, 2528.
- [6] G. Samolyuk, B. P. T. Fokwa, R. Dronskowski, G. J. Miller, *Phys. Rev. B* **2007**, *76*, 094404.
- [7] B. P. T. Fokwa, H. Lueken, R. Dronskowski, *Chem. Eur. J.* **2007**, *13*, 6040.
- [8] STOE Cie., *WinXPOW*, version 1.06, Darmstadt, Germany, 1999.
- [9] G. M. Sheldrick, *SADABS*; University of Göttingen, Germany, 2001.
- [10] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.
- [11] M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov, H. Wondratschek, "Bilbao Crystallographic Server I: Databases and crystallographic computing programs", *Z. Kristallogr.* **2006**, *221*, 15.
- [12] K. Brandenburg, *DIAMOND 3.1e*, Crystal and Molecular Structure Visualization, Crystal Impact GbR, Bonn, 2007.
- [13] E. Raub, E. Roeschel, *Z. Metallkunde*, **1963**, *54*, 455.

- [14] L. Pauling, B. Kamb, *Proc. Natl. Acad. Sci. (USA)* **1986**, 83, 3569.
- [15] T. Lundstroem, *Arkiv for Kemi*, **1969**, 30, 115.
- [16] B. P. T. Fokwa, R. Dronskowski, *J. Alloys Compds.* **2007**, 428, 84.
- [17] B. P. T. Fokwa, J. von Appen, R. Dronskowski, *Chem. Commun.* **2006**, 4419.
- [18] P. Villars, K. Cenzual, Pearson's Crystal Structure Database for Inorganic Compounds (on CD-ROM), Version 1.0, Materials Park, OH, USA, 2007/8.
- [19] B. P. T. Fokwa, R. Dronskowski, *Z. Kristallogr.* **2006**, 221, 445.

#### Figure captions

**Figure 1.** Perspective view along [001] of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ . Boron centered trigonal prisms and  $(\text{Ti/Ru})_2$ -dumbbells (black bonds) are highlighted. The ellipsoids are drawn at 99.9% probability level.

**Figure 2.** (a) Projection nearly along [010] of the crystal structure of  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ : Ruthenium planes perpendicular to [001] are highlighted. (b) Projection nearly along [100] of the crystal structure of  $\text{Ti}_2\text{Rh}_6\text{B}$ : All planes are observed in three directions.

**Table 1**Crystallographic and structure refinement data for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ .

Formula	$\text{Ti}_{10.05(4)}\text{Ru}_{18.95(4)}\text{B}_8$
Formula Weight ( $\text{g}\cdot\text{mol}^{-1}$ );	2483.42;
$F(000)$	2190
Crystal size ( $\text{mm}^3$ )	$0.10 \times 0.03 \times 0.03$
Space group; $Z$	$P4/mbm$ (No. 127); 2
Lattice parameters	$a = 17.591(5) \text{ \AA}$ , $c = 2.9645(13) \text{ \AA}$ $V = 917.4(6) \text{ \AA}^3$
Calc. density ( $\text{g}\cdot\text{cm}^{-3}$ )	8.99
Abs. Correction	Semi-empirical
Abs. Coefficient ( $\text{mm}^{-1}$ )	19.13
$T_{\min}$ ; $T_{\max}$	0.251; 0.598
Diffractometer	Bruker APEX CCD, Mo $K\alpha$ , graphite monochromator
$\theta$ -range	$4.78^\circ < \theta < 36.01^\circ$
$hkl$ -range	$-28 \leq h \leq 17$ $-28 \leq k \leq 28$ $-4 \leq l \leq 4$
No. reflections; $R_{\text{int}}$	9877; 0.0787
No. independent reflections	1266
No. parameters	58
Refinement	<i>SHELX-97</i> , full matrix against $F^2$
$R_1$ ; $wR_2$ (all $I$ )	0.0708; 0.0992
$\text{Goof}$	1.047
Diff. peak / hole ( $\text{e}\cdot\text{\AA}^{-3}$ )	3.253 / $-2.415$

**Table 2**  
Atomic coordinates and equivalent displacement parameters ( $\text{\AA}^2$ ) for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Wyckoffsite	Occupancy	$U_{\text{eq}}^{[\text{a}]} / U_{\text{iso}}$
Ru1	0.91930(4)	0.25328(4)	0	8 <i>i</i>	1.0	0.0068 (2)
Ru2	0.91502(4)	0.41502(4)	0	4 <i>g</i>	1.0	0.0068(2)
Ru3	0.05292(4)	0.32597(4)	0	8 <i>i</i>	1.0	0.0083(2)
Ru4	0.78805(4)	0.16841(4)	0	8 <i>i</i>	1.0	0.0080(2)
Ru5	0.93043(4)	0.09787(4)	0	8 <i>i</i>	1.0	0.0066(2)
Ti1	0.8032(1)	0.3032(1)	1/2	4 <i>h</i>	1.0	0.0081(4)
Ti2/ Ru7	0	0	1/2	2 <i>b</i>	0.97(2)/ 0.03	0.0069(9)
Ti3	0.0352(1)	0.18689(9)	1/2	8 <i>j</i>	1.0	0.0074(3)
Ti4	0.1718 (1)	0.3282(1)	1/2	4 <i>h</i>	1.0	0.0129(5)
Ti5/ Ru6	0.04937(6)	0.45063(6)	1/2	4 <i>h</i>	0.54(2)/ 0.46	0.0109(5)
B1	0. 8775(6)	0.1698(6)	1/2	8 <i>j</i>	1.0	0.010(2)
B2	0.9627(6)	0.3339(6)	1/2	8 <i>j</i>	1.0	0.009(2)

[a]:  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalized  $U_{ij}$  tensors;  $U_{\text{iso}}$  only for boron

**Table 3**  
Selected bond lengths (Å) for  $\text{Ti}_{10}\text{Ru}_{19}\text{B}_8$ .

site <i>i</i>	site <i>j</i>	$d_{ij}$	Coordination <sup>[b]</sup>	site <i>i</i>	site <i>j</i>	$d_{ij}$	coordination <sup>[b]</sup>
Ru1	B2	2.189(8)	2	Ru5	Ti3	2.770(2)	2
	B1	2.212(8)	2		Ru4	2.795(2)	1
	Ti1	2.672(2)	2		Ti3	2.836(2)	2
	Ru3	2.676(2)	1		Ru5	2.964(2)	2
	Ru5	2.741(2)	1	Ti1	Ru1	2.672(2)	4
	Ru4	2.749(2)	1		Ru4	2.808(2)	4
	Ti3	2.778(2)	2		Ti1	2.964(2)	2
	Ru2	2.846(2)	1	Ti2/Ru7	Ru5	2.580(1)	8
Ru2	Ru1	2.964(2)	2		Ti2/Ru7	2.964(2)	2
	B2	2.223(8)	4	Ti3	Ru5	2.770(2)	2
	Ru1	2.846(2)	2		Ru1	2.778(2)	2
	Ti5/Ru6	2.859(1)	4		Ru4	2.808(2)	2
	Ru3	2.888(2)	2		Ru5	2.836(2)	2
Ru3	Ru2	2.964(2)	2		Ru3	2.878(2)	2
	B2	2.175(8)	2	Ti4	Ti3	2.964(2)	2
	Ti4	2.563(2)	2		Ru4	2.527(2)	4
	Ru5/Ti6	2.648(2)	2		Ru3	2.563(2)	4
	Ru1	2.676(2)	1		Ti4	2.964(2)	2
	Ru4	2.855(2)	1	Ti5/Ru6	Ti5/Ru6	2.456(3)	1
	Ti3	2.878(2)	2		Ru3	2.648(2)	4
	Ru2	2.888(2)	1		Ru2	2.859(1)	4
	Ru3	2.964(2)	2		Ti5/Ru6	2.964(2)	2
Ru4	B1	2.162(8)	2	B1	Ru5	2.160(8)	2
	Ti4	2.527(2)	2		Ru4	2.162(8)	2
	Ru5	2.795(2)	1		Ru1	2.212(8)	2
	Ti3	2.808(2)	2	B2	Ru3	2.175(8)	2
	Ti1	2.808(2)	2		Ru1	2.189(8)	2
	Ru3	2.855(2)	1		Ru2	2.223(8)	2
Ru5	Ru4	2.964(2)	2				
	B1	2.160(8)	2				
	Ti2/Ru7	2.580(1)	2				

[b]: number of equivalent contacts between these two sites