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Preparation and crystal structure of the ternary carbides $R_{12}Os_5C_{15}$ with R=Y, Pr, Nd, Sm, Gd–Tm

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Abstract

The title compounds were prepared by arc-melting of the elemental components and subsequent annealing. They crystallize with the hexagonal $La_{12}Re_5C_{15}$-type structure, which was refined for $Tb_{12}Os_5C_{15}$ from X-ray powder diffractometer data: $P\bar{6}2m$, $a=1069.4(1)$ pm, $c=507.95(6)$ pm, $Z=1$, $R_F=0.033$ for 134 structure factors and 12 structural parameters.

Keywords: Crystal structure; Rare earth osmium carbides

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1. Introduction

Many ternary rare earth (R) transition metal (T) carbides have been characterized in recent years, e.g. the series $R_{3.67}TC_6$ with T=Mn, Fe, Ru [1], R_2ReC_2 [2], $R_{12}Mn_5C_{15}$ [3], $R_5Re_2C_7$ [4], $R_{10}Ru_{10}C_{19}$ [5] and references in these publications. With osmium as transition metal component, only three series have been communicated up to now: the series $R_5Os_3C_{4-x}$ with a new kind of filled Mn_5Si_3-type structure [6], R_2OsC_2 [7], which is isotypic with Pr_2ReC_2 [8], and $R_{4-x}Os_{1+y}C_6$ [9] with a structure similar to that of $La_{3.67}FeC_6$ [1]. In the present paper we report on a fourth series of ternary rare earth osmium carbides, which are isotypic with $La_{12}Re_5C_{15}$ [10].

2. Sample preparation, properties and lattice constants

Starting materials were ingots of the rare earth metals, all with nominal purities >99.9%, osmium powder (Degussa, 99.9%, 300 mesh) and graphite flakes (Alfa, >99.5%). Filings of the rare earth elements were prepared under dried (Na) paraffin oil. The oil was removed by dry n-hexane. Because of their reactivity, the filings of yttrium and the early lanthanoids had to be stored under vacuum. They were only briefly exposed to air prior to the reactions.

The compounds were prepared by arc-melting cold-pressed pellets of the elemental components in stoichiometric ratios. Most of the ternary carbides were already present in the quenched ingots; nevertheless, the samples were wrapped in tantalum foil and annealed in evacuated silica tubes for 1 month at 1000°C to enhance their homogeneity, followed by quenching in water. Exceptions were the praseodymium and neodymium compounds, which were obtained only after the arc-melted buttons had been annealed for 4 weeks at 800 and 1000°C, respectively. Hence, these compounds seem to be formed by peritectic reactions.

The carbides of the heavy rare earth elements and yttrium are stable in air for long periods of time, while those with Pr, Nd and Sm as lanthanoid components are sensitive to the humidity of the air. Well crystallized samples have a light grey colour with metallic lustre; the powders are dark grey. Energy dispersive analyses of the samples in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

Guinier powder diagrams of the samples were recorded with Cu $K\alpha_1$ radiation and α-quartz ($a=491.30$ pm, $c=540.46$ pm) as an internal standard. Identification of the diffraction lines was facilitated by intensity calculations [11] using the positional parameters of the refined structure of $Tb_{12}Os_5C_{15}$ (below). The lattice constants, obtained by

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Table 1
Lattice constants of compounds with the hexagonal $La_{12}Re_5C_{15}$-type structure[a]

Compound	*a* (pm)	*c* (pm)	*c*/*a*	*V* (nm^3)
$Y_{12}Os_5C_{15}$	1068.3(2)	503.8(1)	0.4716	0.4979
$Pr_{12}Os_5C_{15}$	1092.8(1)	530.2(1)	0.4852	0.5483
$Nd_{12}Os_5C_{15}$	1089.3(2)	527.4(1)	0.4842	0.5420
$Sm_{12}Os_5C_{15}$	1081.6(1)	518.0(1)	0.4789	0.5248
$Gd_{12}Os_5C_{15}$	1075.6(2)	512.7(1)	0.4767	0.5137
$Tb_{12}Os_5C_{15}$	1069.4(1)	508.0(1)	0.4750	0.5031
$Dy_{12}Os_5C_{15}$	1066.0(2)	504.1(1)	0.4729	0.4961
$Ho_{12}Os_5C_{15}$	1062.3(2)	502.6(1)	0.4731	0.4912
$Er_{12}Os_5C_{15}$	1059.2(1)	498.7(1)	0.4708	0.4845
$Tm_{12}Os_5C_{15}$	1056.1(2)	493.6(1)	0.4674	0.4768

[a] Standard deviations in the positions of the least significant digits are given in parentheses throughout the paper.

least-squares fits, are listed in Table 1. Fig. 1 shows a plot of the cell volumes together with the cell volumes of the isotypic manganese [3] and rhenium compounds [10].

3. Structure refinement of $Tb_{12}Os_5C_{15}$

The crystal structure of $Tb_{12}Os_5C_{15}$ was refined from X-ray powder diffractometer data with the Rietveld method (Fig. 2) using the program FULLPROF [12]. The sample was ground to a fine powder and placed between acetate foils. The intensity data were recorded from a rotating sample on a focusing powder diffractometer (STOE Stadi P) with monochromated Cu Kα_1 radiation, using a linear position-sensitive detector in transmission geometry. Further details of the data collection and the structure refinement are summarized in Table 2.

For the initial least-squares refinement cycles the atomic positions of $La_{12}Re_5C_{15}$ (space group $P\bar{6}2m$ – No. 189, $Z=1$) were used. In the final refinements a total of 22 parameters was optimized, including the zero point, the scale factor, the lattice constants of $Tb_{12}Os_5C_{15}$, two asymmetry parameters and four parameters to fit the peak profile with a pseudo-Voigt function. The terbium and osmium atoms were each refined with a common isotropic displacement parameter, while the displacement parameters of the carbon atoms were held constant at a reasonable value. The goodness of fit (χ^2) was 3.43, while the residuals amounted to $R_{Bragg}=0.046$ and $R_F=0.033$ for the 134 structure factors. The atomic parameters are listed in Table 3 and the interatomic distances in Table 4.

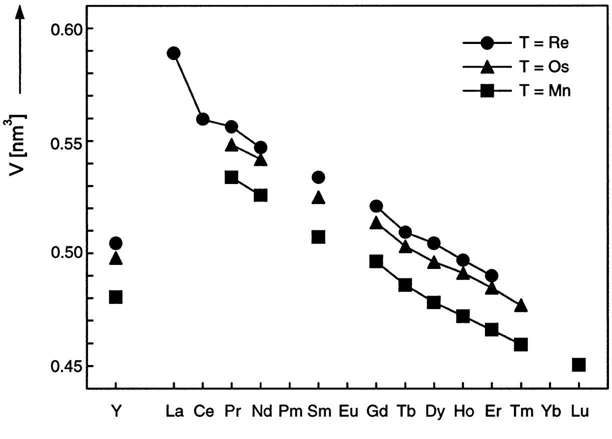

Fig. 1. Cell volumes of $La_{12}Re_5C_{15}$-type carbides.

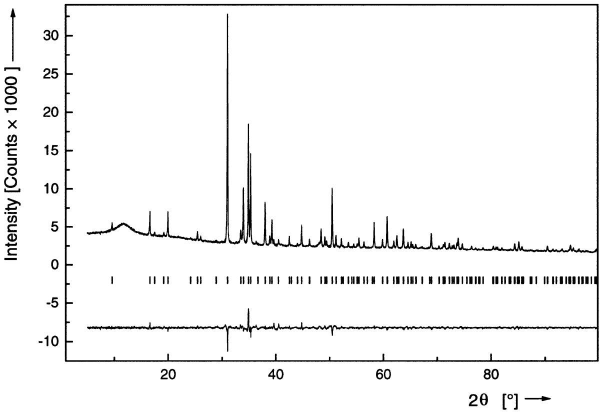

Fig. 2. Rietveld refinement plot for $Tb_{12}Os_5C_{15}$. The peak positions and the difference profile between the calculated and the observed plots are shown in the lower part of the figure.

Table 2
Crystallographic data for $Tb_{12}Os_5C_{15}$

Lattice constants	Table 1
Formula units/cell	$Z=1$
Space group	$P\bar{6}2m$ (No. 189)
Formula mass	3038.3
Calculated density (g/cm^3)	10.03
Range in 2θ (deg)	5–100
Step width in 2θ (deg)	0.02
Total measuring time (h)	23
Total number of steps	4751
Number of reflections	134
Number of structural parameters	12
Goodness of fit (χ^2)	3.43
Bragg residual	$R_{Bragg}=0.046$
Conventional residual	$R_F=0.033$

Table 3
Atomic parameters of $Tb_{12}Os_5C_{15}^a$

Atom	$P\bar{6}2m$	*x*	*y*	*z*	*B*
Tb1	6j	0.2749(4)	0.4598(3)	0	0.39(5)
Tb2	3g	0.4291(4)	0	1/2	0.39
Tb3	3g	0.7919(4)	0	1/2	0.39
Os1	3f	0.1553(3)	0	0	0.42(5)
Os2	2d	1/3	2/3	1/2	0.42
C1	6k	0.273(6)	0.469(5)	1/2	0.8
C2	3f	0.331(5)	0	0	0.8
C3	3f	0.458(5)	0	0	0.8
C4	3f	0.813(7)	0	0	0.8

[a] The last column contains the isotropic thermal parameters ($\times 10^4$, in units of pm^2) of the metal atoms. The corresponding parameters of the carbon atoms were held at the indicated values.

Table 4
Interatomic distances in the structure of $Tb_{12}Os_5C_{15}^{a}$

Tb1:	1C3	253(4)	Tb3:	2C1	252(4)	C1:	1Os2	188(4)
	2C1	254.2(2)		2C4	255.0(1)		1Tb3	252(4)
	1C2	255(5)		4Os1	323.5(2)		2Tb1	254.2(2)
	1C4	257.9(3)		4Tb1	350.5(3)		1Tb2	273(5)
	1C3	293(4)		2Tb3	385.5(5)		1Tb2	280(4)
	1Os1	311.0(3)		1Tb2	388.0(6)	C2:	1C3	136(8)
	2Os2	321.8(2)		2Tb2	397.5(5)		1Os1	188(5)
	2Tb1	342.1(4)	Os1:	2C4	185.4(2)		2Tb1	255(5)
	1Tb1	342.5(4)		1C2	188(5)		2Tb2	275(2)
	2Tb3	350.5(3)		2Os1	287.7(4)	C3:	1C2	136(8)
	2Tb2	375.8(4)		2Tb1	311.0(3)		2Tb1	253(4)
	2Tb2	377.3(3)		4Tb3	323.5(2)		2Tb2	255.9(7)
Tb2:	2C3	255.9(7)		2Tb2	387.6(4)		2Tb1	293(4)
	2C1	273(5)	Os2:	3C1	188(4)	C4:	2Os1	185.4(2)
	2C2	275(2)		3Tb2	317.9(3)		2Tb3	255.0(1)
	2C1	280(4)		6Tb1	321.8(2)		2Tb1	257.9(3)
	2Os2	317.9(3)						
	4Tb1	375.8(4)						
	4Tb1	377.3(3)						
	2Os1	387.6(4)						
	1Tb3	388.0(6)						
	2Tb3	397.5(5)						

[a] All distances shorter than 410 pm (metal-metal), 320 pm (metal-carbon) and 300 pm (carbon-carbon) are listed.

4. Discussion

The presently reported carbides with $La_{12}Re_5C_{15}$-type structure are the first of this structure type with osmium as transition metal component. They are represented in Fig. 1 by their cell volumes together with the other $La_{12}Re_5C_{15}$-type carbides formed with manganese and rhenium. The cell volumes of the osmium-containing compounds are in all cases in between those of the manganese and rhenium compounds. We have not yet been successful in preparing such osmium containing carbides with lanthanum, cerium, ytterbium or lutetium.

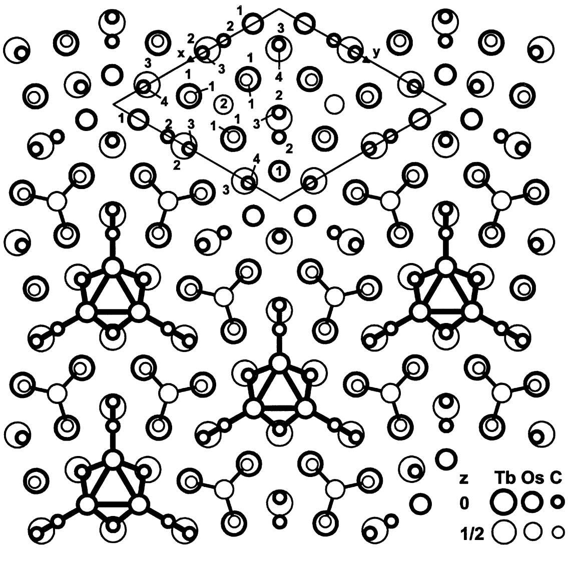

Fig. 3. The $La_{12}Re_5C_{15}$-type structure of $Tb_{12}Os_5C_{15}$. Single-digit numbers correspond to the atom designations. The trigonal-planar polyanionic groups $(Os1)_3(C4)_3(C2{=}C3)_3$ and $Os2(C1)_3$ are emphasized in the lower part of the figure.

The crystal structure of $Tb_{12}Os_5C_{15}$ is shown in Fig. 3 emphasizing the two kinds of osmium–carbon polyanions, which have trigonal symmetry, and which are separated from each other by terbium cations. Chemical bonding in the $La_{12}Re_5C_{15}$-type carbides has already been discussed, and it was shown that the coordinations of the rhenium atoms are compatible with the 18-electron rule [10]. In the presently reported osmium compounds the electron count is higher. It would be of interest to see how this higher electron count is reflected by the interatomic distances. Unfortunately, the most important interatomic distances are those between the metal atoms and the light carbon atoms. These distances are affected by the relatively large standard deviations of the carbon positions and the differences in the interatomic distances are not of sufficient significance to justify a detailed discussion. This is also the case for the C–C distances in those four compounds, where the structures have been refined. These distances were found to be 129(10), 142(5), 132(3) and 136(8) pm in $La_{12}Re_5C_{15}$ [10], $Ho_{12}Re_5C_{15}$ [10], $Dy_{12}Mn_5C_{15}$ [3] and the presently reported carbide $Tb_{12}Os_5C_{15}$, respectively. Nevertheless, these distances are all in between the C–C triple-bond distance of 120 pm and the C–C single-bond distance of 154 pm observed in hydrocarbons. The average of 135 pm corresponds (admittedly somewhat by accident) exactly to a C–C double-bond.

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