The Lanthanoid Osmium Gallides $Er_2Os_3Ga_{10}$ and $Tm_2Os_3Ga_{10}$ with $Yb_2Ru_3Ga_{10}$-type Structure

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The title compounds were prepared by melting and annealing of stoichiometric mixtures of the elemental components in a high-frequency furnace. They are isotypic with $Yb_2Ru_3Ga_{10}$ ($P4/mbm$, $Z = 2$). Their lattice constants were determined from X-ray powder data, and their crystal structures were refined from single-crystal X-ray data. $Er_2Os_3Ga_{10}$: $a = 883.4(1)$, $c = 636.7(1)$ pm, $R = 0.025$ for 506 F_o values, and $Tm_2Os_3Ga_{10}$: $a = 883.2(1)$, $c = 633.6(1)$ pm, $R = 0.023$ for 568 F_o values and 25 variable parameters each. The crystal structures of these intermetallic compounds are briefly discussed.

Key words: Rare Earth Metal Compounds, Osmium Intermetallics, Gallides

Introduction

The literature on intermetallic gallium compounds has been reviewed by Yuri Grin, who has also greatly contributed to the structural chemistry of these intermetallics [1]. Some years ago we have investigated ternary compounds of rare earth elements (*Ln*) with transition metals (*T*) and with a high content of gallium. We reported on the series $Ln_2Ru_3Ga_9$ [2] with $Y_2Co_3Ga_9$-type structure [3], $LnRu_2Ga_8$ [4] with $CaCo_2Al_8$-type structure [5], and $LnOsGa_3$ [6] with $TmRuGa_3$-type structure [7]. We have found new structure types for the series $Ln_2Ru_3Ga_{10}$ [4], $LnOsGa_4$ [6] and $Ln_3Ru_4Ga_{15}$ [8], and for the compound $Sm_2Ru_2Ga_9$ [9].

Other rare earth transition metal gallides with a high content of gallium investigated recently include Sm_2NiGa_{12} [10], $Yb_4Ni_{10+x}Ga_{21-x}$ [11], $YbAgGa_2$ [12], $Y_3Cu_4Ga_7$ [13], $YbNiGa_4$ [14], and $Eu_2T_3Ga_9$ (T = Rh, Ir) [15]. Many other new compounds with a high content of gallium have been prepared in recent years using gallium as a flux [16]. Here we report on two new gallides with $Yb_2Ru_3Ga_{10}$-type structure [4]. A preliminary account of this work has been published earlier [17].

Experimental Section

Sample preparation, properties, and lattice constants

The compounds were prepared from the elemental components (all with nominal purity > 99.9 %) with the ideal
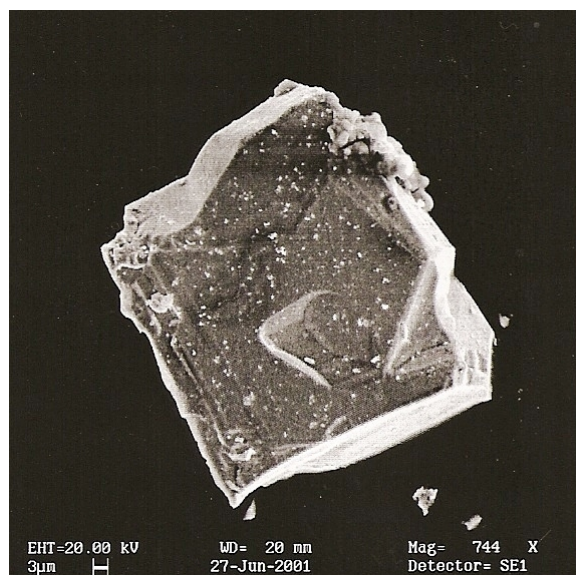

Fig. 1. A scanning electron micrograph of a $Tm_2Os_3Ga_{10}$ crystal.

atomic ratio 2 : 3 : 10. The rare earth elements were puchased in the form of ingots which were cut to pieces. Osmium (Merck) was obtained in powder form. Gallium ingots (Heraeus) were crushed to small pieces at liquid nitrogen temperature. The cold-pressed pellets (total weight ~0.5 g) were placed in alumina crucibles which in turn were sealed in silica tubes under an atmosphere of purified argon (~600 mbar). The silica tubes were cooled on the outside

Table 1. Lattice parameters of the new osmium-containing tetragonal $Yb_2Ru_3Ga_{10}$-type gallides as determined from Guinier powder diagrams. For comparison, the lattice constants of the earlier reported ruthenium compounds [4] are also listed.

Compound	a (pm)	c (pm)	c/a	V (nm³)
$Er_2Os_3Ga_{10}$	883.4(1)	636.7(1)	0.7207	0.4968
$Tm_2Os_3Ga_{10}$	883.2(1)	633.6(1)	0.7174	0.4943
$Yb_2Ru_3Ga_{10}$	881.9(1)	632.5(1)	0.7172	0.4919
$Lu_2Ru_3Ga_{10}$	881.7(1)	630.7(1)	0.7153	0.4902

with flowing water and, the samples were heated in the sample chamber of a high-frequency furnace until an exothermic reaction (at approximately 1000 °C) was observed. Subsequently the temperature was raised briefly two or three times to 1500 °C to increase the homogeneity of the sample, and then lowered to a temperature just below melting. At that temperature the sample was kept for approximately 6 h to enhance the growth of relatively large grains. Then the samples were cooled to r. t. within one minute.

The compounds are stable on air for long periods of time. Crystals are plate-like (Fig. 1) with metallic luster. They can easily be ground to dark gray powders. Energy-dispersive X-ray fluorescence analyses of the samples in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

Guinier powder diagrams of all products were recorded with monochromatized Cu$K_{\alpha1}$ radiation using α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The proper assignment of indices was aided by comparing the observed patterns with the theoretical ones [18], calculated with the atomic positions of $Yb_2Ru_3Ga_{10}$ [4]. The lattice constants (Table 1) are the results of least-squares fits.

Structure refinements from single-crystal X-ray data

Small, well-shaped single crystals of $Er_2Os_3Ga_{10}$ and $Tm_2Os_3Ga_{10}$ were selected for the structure determinations. Their quality for the X-ray data collections was checked on the basis of Laue diffractograms recorded on a precession camera with unfiltered Mo radiation. The X-ray intensity data were measured on an Enraf Nonius four-circle diffractometer (CAD4) with graphite-monochromatized MoK_{α} radiation and a scintillation counter with pulse-height discrimination. The scans were along the diffraction streaks ($\theta/2\theta$) with background counts at both ends of each scan. More details of the data collections are listed in Table 2. Empirical absorption corrections were applied on the basis of ψ-scan data.

The isotypy of the crystal structures with that of $Yb_2Ru_3Ga_{10}$ [4] was already suspected on the basis of the powder data. The high Laue symmetry was confirmed prior to the data averaging, and the positional parameters of

Table 2. Details of the single-crystal data collections and structure refinements of $Er_2Os_3Ga_{10}$ and $Tm_2Os_3Ga_{10}$. $Yb_2Ru_3Ga_{10}$-type structure, space group $P4/mbm$ (no. 127), $Z = 2$.

Empirical formula	$Er_2Os_3Ga_{10}$	$Tm_2Os_3Ga_{10}$
Formula mass	1602.3	1605.7
Unit cell dimensions (single crystal)		
a, pm	883.3(1)	883.4(1)
c, pm	636.6(1)	633.7(1)
V, nm³	0.4967	0.4943
Calculated density, g cm⁻³	10.71	10.79
Crystal size, μm³	$40 \times 40 \times 40$	$40 \times 50 \times 60$
Transmission ratio (max/min)	2.01	4.51
Absorption coefficient, mm⁻¹	81.4	82.8
$F(000)$, e	1348	1352
Range in 2θ, deg	$4-70$	$4-70$
Range in hkl	$\pm14/\pm14/$	$\pm14/\pm14/$
	-10 to $+1$	-10 to $+2$
Total no. reflections	5044	5423
Independent reflections / R_{int}	634 / 0.113	633 / 0.129
Reflections with $I \geq 2\sigma(I)$ / R_{σ}	506 / 0.049	568 / 0.051
Number of ref. variables	25	25
Goodness-of-fit on F^2	1.177	1.135
Final residuals		
$R1$ [$F \geq 2\sigma(F)$]	0.025	0.023
$wR2$ [$I \geq 2\sigma(I)$]	0.059	0.053
$R1$ (all data)	0.042	0.027
Largest diff. peak / hole, e Å⁻³	$+5.9 / -4.2$	$+3.3 / -2.9$

$Yb_2Ru_3Ga_{10}$ were used as starting parameters for the structure refinements with a full-matrix least-squares program [19] using atomic scattering factors, corrected for anomalous dispersion, as provided by the program. The weighting scheme accounted for the counting statistics, and a parameter correcting for isotropic extinction was optimized as a least-squares variable.

In order to check the compositions of the crystals we refined occupancy values together with variable isotropic displacement parameters. This was possible because we had been collecting diffraction data up to rather high 2θ values (70°). The results varied between 98.8(1.2) % for Ga1 and 101.0(0.7) % for Os2 in $Er_2Os_3Ga_{10}$ and between 99.0(1.0) % for Ga1 and 101.0(1.0) % for Ga2 in $Tm_2Os_3Ga_{10}$, and all occupancy parameters were within 2 standard deviations at the ideal values. Thus, we used the ideal occupancy values during the final least-squares cycles. The final residuals are summarized in Table 2. The positional atomic parameters were standardized using the program STRUCTURE TIDY [20]. They are listed in Table 3. Table 4 shows the interatomic distances.

Details of the crystal structure investigations may also be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html)

Table 3. Atomic positions and isotropic displacement parameters (pm^2) of $Er_2Os_3Ga_{10}$ and $Tm_2Os_3Ga_{10}$ (space group *P4/mbm* (no. 127), $Z = 2$). The structures were refined with anisotropic displacement parameters. Listed are the equivalent isotropic parameters U_{eq} (Å^2), which are defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*P4/mbm*	x	y	z	U_{eq}
			$Er_2Os_3Ga_{10}$:		
Er	4*g*	0.18273(5)	$1/2+x$	0	0.43(1)
Os1	4*h*	0.17859(4)	$1/2+x$	$1/2$	0.25(1)
Os2	2*a*	0	0	0	0.25(1)
Ga1	16*l*	0.06127(8)	0.20654(9)	0.29269(13)	0.44(1)
Ga2	4*f*	0	$1/2$	0.28402(26)	0.50(2)
			$Tm_2Os_3Ga_{10}$:		
Tm	4*g*	0.18324(3)	$1/2+x$	0	0.57(1)
Os1	4*h*	0.17843(4)	$1/2+x$	$1/2$	0.38(1)
Os2	2*a*	0	0	0	0.37(1)
Ga1	16*l*	0.06125(6)	0.20676(6)	0.29255(7)	0.56(1)
Ga2	4*f*	0	$1/2$	0.28252(15)	0.63(2)

Table 4. Interatomic distances (pm) in the structures of the gallides $Ln_2Os_3Ga_{10}$ (Ln = Er/Tm) with the lattice constants as calculated from the powder data. All distances shorter than 360 pm are listed. Standard deviations are all equal to or less than 0.2 pm.

Ln:	2Ga2	291.2/290.6	Ga1:	Ga1	264.0/262.9
	4Ga1	293.8/292.8		Ga2	264.9/264.7
	4Ga1	301.3/300.7		Os1	266.2/266.0
	Os1	318.4/316.9		Os2	266.4/265.8
	Os2	323.4/323.2		2Ga1	269.2/269.3
Os1:	2Ga2	262.1/262.0		Os1	269.5/269.0
	4Ga1	266.2/266.0		Ga1	290.1/289.8
	4Ga1	269.5/269.0		Ln	293.8/292.8
	2Ln	318.4/316.9		Ln	301.3/300.7
Os2:	8Ga1	266.4/265.8	Ga2:	2Os1	262.1/260.0
	4Ln	323.4/323.2		4Ga1	264.9/264.7
				Ga2	275.0/275.6
				2Ln	291.2/290.6
				Ga2	361.7/358.0

on quoting the deposition number CSD-420594 ($Er_2Os_3Ga_{10}$) and CSD-420595 ($Tm_2Os_3Ga_{10}$).

Discussion

Aside from the presently reported osmium gallides $Er_2Os_3Ga_{10}$ and $Tm_2Os_3Ga_{10}$ only two more compounds are now known to crystallize with this structure type, both with ruthenium as transition metal component: $Lu_2Ru_3Ga_{10}$ [4] and the prototype $Yb_2Ru_3Ga_{10}$ [4]. Interestingly, the rare earth metal components of these four gallides follow the sequence as these rare earth metals occur in the periodic system. The unit cell volume of these four compounds decreases almost monotonically (Table 1). Or with other words: the decrease in the cell volumes due
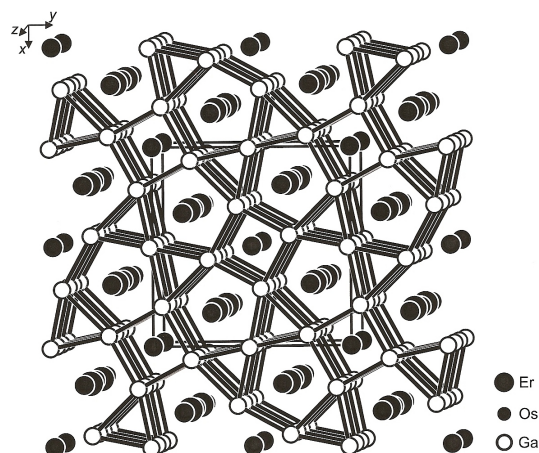

Fig. 2. Crystal structure of $Er_2Os_3Ga_{10}$ in a projection approximately along the tetragonal axis emphasizing Ga–Ga bonds within the network extending perpendicular to the tetragonal axis.
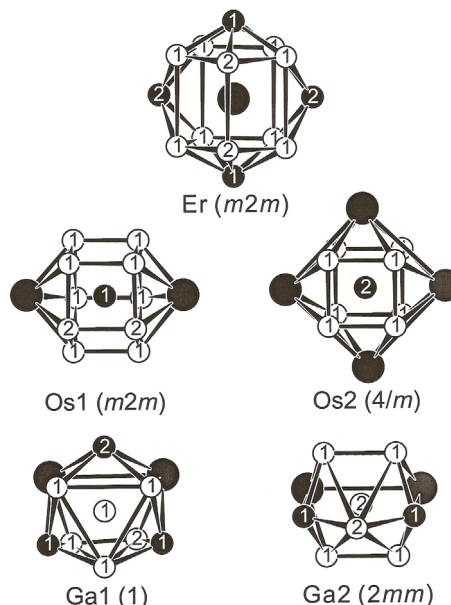

Fig. 3. Near-neighbor environments in the structure of $Er_2Os_3Ga_{10}$. Single-digit numbers correspond to the atom designations. The site symmetries of the central atoms are indicated in parentheses.

to the rare earth components is dominant. Thus, the ruthenium and osmium atoms seemingly have very similar size. For exactly isotypic compounds, however, the Ru compounds have slightly smaller cell volumes. For instance, the cell volume of RuP_4 is smaller by 0.4 % than that of OsP_4 [21], and for the series $Ln_3T_4Al_{12}$ (T = Ru, Os) the cell volumes of

the Ru compounds are smaller by 0.7 % on average than those of the corresponding Os compounds [22]. The cell volume of $Yb_2Ru_3Ga_{10}$ is only slightly larger than that of the isotypic Lu compound (Table 1), thus indicating that the ytterbium atoms in $Yb_2Ru_3Ga_{10}$ are essentially trivalent. A considerably larger cell volume would be expected if the Yb atoms were divalent.

In view of the similar atomic sizes it is not surprising that the differences in the interatomic distances of $Tm_2Os_3Ga_{10}$ on the one hand and $Yb_2Ru_3Ga_{10}$ [4] on the other hand are rather small. The largest difference occurs for one relatively weekly bonding Ga2–Ga2 distance which amounts to 275.6 pm in the Tm compound and 272.9 pm in the Yb compound. All other differences between corresponding interatomic distances of near neighbors in the two structures amount to 1 pm or less.

The structure of these compounds is shown in Fig. 2 with $Er_2Os_3Ga_{10}$ as a representative. It is clearly dominated by the many Ga–Ga interactions. The coordination polyhedra are displayed in Fig. 3. We have discussed the crystal structure of the prototype $Yb_2Ru_3Ga_{10}$ earlier, and the reader is referred to that paper for a detailed discussion of the structure [4].

We emphasize again that the structure contains two rather different sites for the transition metals. The Os1 atom is situated in a pentagonal prism formed by Ga atoms with two rare earth metal atoms outside the pentagonal faces of the prism, thus increasing the coordination number (CN) to 12. A similar coordination was already observed for one of the three Cr sites in the $CeCr_2Al_{20}$-type structure [23], which has some 100 representatives, including many compounds where the positions of the Al atoms are occupied by Zn atoms [24]. A corresponding coordination also occurs for the Co atoms in the $Gd_2Co_3Zn_{14}$-type structure, which again has many representatives $Ln_2T_3Zn_{14}$ (T = Fe, Co, Rh, Ni, Pd, Pt) [25].

The other Os site of $Er_2Os_3Ga_{10}$, the Os2 site, also has CN 12, however, with 8 Ga atoms forming a cube which is capped by 4 Er atoms (Fig. 3). A similar coordination has already been found for one of the two Co sites in $Y_2Co_3Ga_9$ [3], for the Pt5 atoms in $Er_4Pt_9Al_{24}$ [26], for the Ru and Os atoms in $TmRuGa_3$ [7] and $TbOsGa_3$ [6], respectively, and for the Os2 atoms in $CeOsGa_4$ [6].

In concluding, we remark that the investigations of ternary systems of lanthanum and the lanthanoids with transition metals and with a high content of aluminum or gallium have resulted in many new compounds. Nevertheless, we are convinced that many more new compounds remain to be prepared and characterized. It is somewhat surprising that few of the ternary gallides are isotypic with the corresponding aluminides. For instance, there are more than 80 aluminides $Ln_6T_4Al_{43}$ with $Ho_6Mo_4Al_{43}$-type structure [27, 28], and up to now, to our knowledge, no gallides with this structure have been reported. The dissimilarity in the structures of compounds with a high content of aluminum and gallium is of course already manifested in the structures of the elements. Aluminum has a simple cubic face-centered (A1) type structure, while gallium crystallizes with a rather complicated orthorhombic structure with one relatively short Ga−Ga bond [29].

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