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Solid solutions of Ti in the binary compounds R_3Ga_2 (R = Y, Er)

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The crystal structures of two samples belonging to the substitutional solid solutions of Ti (1.6 at.% at 600°C) in the binary gallides Y_3Ga_2 and Er_3Ga_2 were refined from X-ray powder diffraction data. Both solid solutions belong to the structure type Gd_3Ga_2: Pearson symbol *tI*80, space group *I*4/*mcm*, a = 11.6264(11), c = 14.8543(14) Å for $Y_{2.97(1)}Ti_{0.08(2)}Ga_{1.95(1)}$ and a = 11.4577(9), c = 14.6999(12) Å for $Er_3Ti_{0.08(2)}Ga_{1.92(2)}$. In the former case titanium atoms substitute for both Y and Ga atoms (icosahedral and cubic coordination, respectively), whereas in the latter case the titanium atoms exclusively substitute for Ga atoms (cubic coordination).

Rare-earth metals / Titanium / Gallium / X-ray powder diffraction / Solid solution / Crystal structure

Introduction

Investigations of the systems {Y, Er}–Ti–Ga [1,2], which resulted in the construction of the isothermal sections of the phase diagrams at 800ºC, revealed the existence of two compounds in each system, RTi$_2$Ga$_4$ and R_4TiGa$_3$. The crystal structure of the ternary compounds RTi$_2$Ga$_4$ belongs to the type YbMo$_2$Al$_4$ (Pearson symbol *tI*14, space group *I*4/*mmm*, a = 6.712, c = 5.484 Å for R = Y [1] and a = 6.706, c = 5.470 Å for R = Er [3]). The crystal structure of the other two compounds remained undetermined. The aim of the present investigation was the synthesis and structural investigation of the "R_4TiGa$_3$" phases.

Experimental

Alloys of nominal composition $R_{50}Ti_{12.5}Ga_{37.5}$ (R = Y, Er) were synthesized from high-purity metals ($R \geq$ 99.9 wt.%, Ti $\geq$ 99.7 wt.%, Ga $\geq$ 99.99 wt.%) by arc melting in a water-cooled copper crucible under a purified argon atmosphere, using a tungsten electrode. To achieve good homogeneity the samples were melted twice. The alloys were then annealed in evacuated silica ampoules at 600ºC or 500ºC for two months, and subsequently quenched in cold water. The loss during the preparation of the samples was less than 0.5% of the total mass, which was 1 g for each alloy.

X-ray powder diffraction patterns of the samples were obtained at room temperature, on a diffractometer Stoe Stadi P with a linear position-sensitive detector and Cu $K\alpha_1$-radiation (range 6-93º 2θ, step size 0.015°; alloys annealed at 600ºC) or DRON-2.0M with Fe $K\alpha$-radiation (range 15-140º 2θ, step size 0.05°; alloys annealed at 500ºC). The X-ray phase analysis was carried out using the WinXPow program package [4] and the structures were refined by the full-profile Rietveld method using the FullProf Suite program package [5].

Results

The X-ray phase analysis did not confirm the existence of individual ternary compounds of composition R_4TiGa$_3$ in the systems {Y, Er}–Ti–Ga, neither at 500 nor at 600ºC. Instead, substitutional solid solutions based on the binary compounds R_3Ga_2 were found.

The binary compounds R_3Ga_2 (R = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) were discovered in 1986 [6], a few years after the investigation of the phase diagrams of the systems {Y, Er}–Ti–Ga. Their crystal structures are described by the prototype Gd_3Ga_2 (Pearson symbol *tI*80, space group *I*4/*mcm*).

The starting atom coordinates for the main phases in the synthesized alloys were taken from the structure of Gd_3Ga_2 [6]. In the final cycles of the refinements the following parameters were allowed to vary: sample shift, scale factors, cell parameters, profile parameters (pseudo-Voigt profile function), atom positional and displacement parameters, and preferred orientation parameters. The isotropic displacement parameters of atoms of the same chemical element

were constrained to be equal. The background was defined by linear interpolation between manually assigned points. The sample $Y_{50}Ti_{12.5}Ga_{37.5}$ annealed at 600ºC was three-phase and contained, in addition to the main phase $Y_{2.97(1)}Ti_{0.08(2)}Ga_{1.95(1)}$, binary Ti_3Ga [7] and small amounts of an unidentified phase. In the sample $Er_{50}Ti_{12.5}Ga_{37.5}$ annealed at 600ºC, three phases were identified: $Er_3Ti_{0.08(2)}Ga_{1.92(2)}$, Er_5Ga_3 [8], and Ti_3Ga [7]. For the secondary phases only the scale factors and cell parameters were refined independently, whereas the profile parameters were constrained to those of the main phases, and the structural parameters were fixed to the values reported in the literature. Experimental, calculated and the difference between the experimental and calculated X-ray powder diffraction patterns of the samples $Y_{50}Ti_{12.5}Ga_{37.5}$ and $Er_{50}Ti_{12.5}Ga_{37.5}$ are shown in Figs. 1,2. Experimental details and crystallographic data are listed in Tables 1,2, and atom coordinates and isotropic displacement parameters for the Gd_3Ga_2-type phases are given in Tables 3,4. The refinements carried out on the samples annealed at 500ºC showed the same distribution of atoms in the ternary Gd_3Ga_2-type phases as for the samples annealed at 600ºC. The cell parameters at 500ºC are: a = 11.5706(16), c = 14.826(2) Å for R = Y and a = 11.4238(11), c = 14.6763(17) Å for R = Er [9].

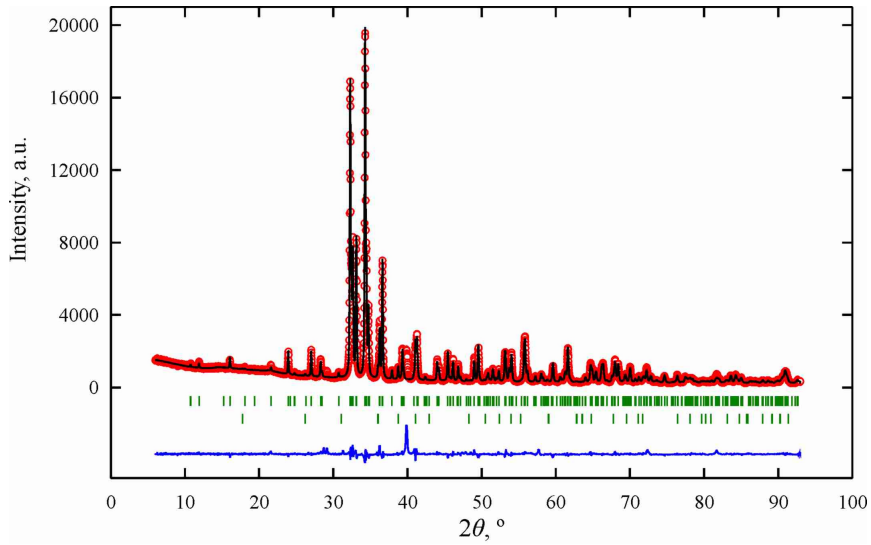

Fig. 1 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Y_{50}Ti_{12.5}Ga_{37.5}$ annealed at 600ºC (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of reflections from $Y_{2.97(1)}Ti_{0.08(2)}Ga_{1.95(1)}$ and Ti_3Ga. The strongest peak of the unidentified phase is at 39.9º 2θ.

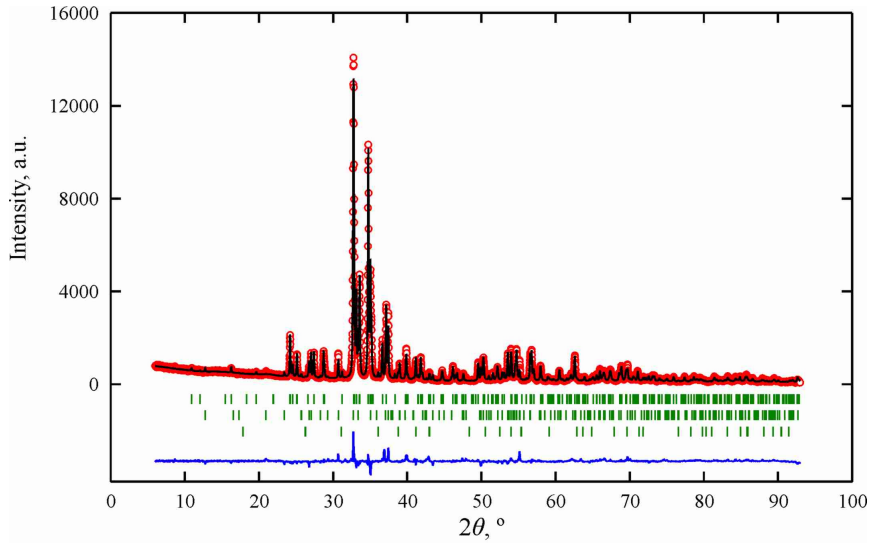

Fig. 2 Experimental (circles), calculated (continuous line) and difference between experimental and calculated (bottom) X-ray powder diffraction patterns of the sample $Er_{50}Ti_{12.5}Ga_{37.5}$ annealed at 600ºC (Cu $K\alpha_1$-radiation). Vertical bars indicate the positions of reflections from $Er_3Ti_{0.08(1)}Ga_{2.92(1)}$, Er_5Ga_3, and Ti_3Ga.

Table 1 Experimental details and crystallographic data for the individual phases in the sample $Y_{50}Ti_{12.5}Ga_{37.5}$ annealed at 600ºC.

Phase		$Y_{2.97(1)}Ti_{0.08(2)}Ga_{1.95(1)}$	Ti_3Ga
Content, wt.%		93.8(6)	6.2(1)
Structure type		Gd_3Ga_2	Mg_3Cd
Pearson symbol		*tI*80	*hP*8
Space group		*I*4/*mcm* (#140)	$P6_3/mmc$ (#194)
Cell parameters:	*a*, Å	11.6264(11)	5.7513(6)
	c, Å	14.8543(14)	4.6435(6)
Cell volume *V*, Å^3		2007.9(3)	133.02(3)
Number of formula units in the cell *Z*		16	2
Density D_X, g cm^{-3}		5.345	5.329
Preferred orientation: value / [direction]		0.932(4) / [001]	0.938(11) / [110]
Reliability factors:	R_B	0.0685	0.114
	R_F	0.0484	0.0423
Profile parameters	*U*	0.077(10)	
	V	0.008(9)	
	W	0.009(2)	
Shape parameter		0.696(8)	
Asymmetry parameters		0.047(9), 0.0046(14)	
Reliability factors:	R_p	0.0474	
	R_{wp}	0.0876	
	χ^2	6.41	

Table 2 Experimental details and crystallographic data for the individual phases in the sample $Er_{50}Ti_{12.5}Ga_{37.5}$ annealed at 600ºC.

Phase		$Er_3Ti_{0.08(2)}Ga_{1.92(2)}$	Er_5Ga_3	Ti_3Ga
Content, wt.%		72.0(5)	23.1(2)	4.9(1)
Structure type		Gd_3Ga_2	Ba_5Si_3	Mg_3Cd
Pearson symbol		*tI*80	*tP*32	*hP*8
Space group		*I*4/*mcm* (#140)	*P*4/*ncc* (#130)	$P6_3/mmc$ (#194)
Cell parameters:	*a*, Å	11.4577(9)	7.5892(6)	5.7418(6)
	c, Å	14.6999(12)	13.8545(12)	4.6415(7)
Cell volume *V*, Å^3		1929.8(3)	797.96(11)	132.52(3)
Formula units per cell *Z*		16	4	2
Density D_X, g cm^{-3}		8.804	8.703	5.349
Preferred orientation: value / [direction]		0.972(5) / [001]	0.978(6) / [001]	0.999(19) / [110]
Reliability factors:	R_B	0.0776	0.160	0.0776
	R_F	0.0822	0.121	0.0771
Profile parameters	*U*		0.029(7)	
	V		0.005(7)	
	W		0.0117(14)	
Shape parameter			0.727(9)	
Asymmetry parameters			0.066(7), 0.0081(15)	
Reliability factors:	R_p		0.0677	
	R_{wp}		0.101	
	χ^2		4.65	

Discussion

The two gallides Y_3Ga_2 and Er_3Ga_2 dissolve similar amounts of Ti (1.6 at.% at 600ºC). However, the distribution of the Ti atoms in the structures is different. In the structure of $Er_3Ti_{0.08(2)}Ga_{1.92(2)}$ the titanium atoms partly substitute for the smaller Ga atoms in Wyckoff position 4*c*, forming a statistical mixture 0.33(6)Ti + 0.67(6)Ga. This leads to an increase of the cell parameters as compared to those of binary Er_3Ga_2 (a = 11.385, c = 14.54 Å at 600ºC [6]).

Table 3 Atom coordinates and isotropic displacement parameters for $Y_{2.97(1)}Ti_{0.08(2)}Ga_{1.95(1)}$ (structure type Gd_3Ga_2, *tI*80, *I*4/*mcm*).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Y1	32*m*	0.06652(14)	0.20356(16)	0.13608(10)	0.55(3)
Y2	8*h*	0.1693(3)	0.6693(3)	0	0.55(3)
Y3[a]	8*g*	0	½	0.1464(3)	0.55(3)
Ga1	16*l*	0.1778(2)	0.6778(2)	0.1995(2)	0.73(6)
Ga2	8*h*	0.6169(3)	0.1169(3)	0	0.73(6)
Ga3[b]	4*c*	0	0	0	0.73(6)
Ga4	4*a*	0	0	¼	0.73(6)

[a] Y3 = 0.94(1)Y + 0.06(1)Ti; [b] Ga3 = 0.19(4)Ti + 0.81(4)Ga.

Table 4 Atom coordinates and isotropic displacement parameters for $Er_3Ti_{0.08(2)}Ga_{1.92(2)}$ (structure type Gd_3Ga_2, *tI*80, *I*4/*mcm*).

Site	Wyckoff position	*x*	*y*	*z*	B_{iso}, Å^2
Er1	32*m*	0.06623(16)	0.20329(17)	0.13621(12)	0.40(4)
Er2	8*h*	0.1689(3)	0.6689(3)	0	0.40(4)
Er3	8*g*	0	½	0.1462(3)	0.40(4)
Ga1	16*l*	0.1788(4)	0.6788(4)	0.2003(4)	0.88(10)
Ga2	8*h*	0.6172(6)	0.1172(6)	0	0.88(10)
Ga3[a]	4*c*	0	0	0	0.88(10)
Ga4	4*a*	0	0	¼	0.88(10)

[a] Ga3 = 0.33(6)Ti + 0.67(6)Ga.

In the structure of $Y_{2.97(1)}Ti_{0.08(2)}Ga_{1.95(1)}$ titanium atoms partly substitute for Ga atoms in Wyckoff position 4*c* (0.19(4)Ti + 0.81(4)Ga). However, Ti atoms also replace the larger Y atoms in Wyckoff position 8*g*, forming a statistical mixture 0.94(1)Y + 0.06(1)Ti. In this case the cell parameters do not change significantly with respect to those of binary Y_3Ga_2 (a = 11.62, c = 14.86 Å at 600ºC [6]).

The content of one unit cell and coordination polyhedra for the structure of $Er_3Ti_{0.08(2)}Ga_{1.92(2)}$ are shown in Fig. 3. The Er sites have the coordination numbers 15 (Er1, Er2) and 13 (Er3). The corresponding polyhedra are: pentagonal prisms of composition $GaEr_9$ and Er_{10} (for Er1 and Er2, respectively) with five Ga atoms capping the two base and three side faces, and an icosahedron Ga_6Er_6 with one additional Er atom (for Er3). The Ga sites have the coordination numbers 10 (Ga1, Ga2) and 8 (Ga3, Ga4) and the following polyhedra: square antiprisms Er_8, without capping atoms (for site Ga4), or with one Ga and one additional Er atom capping the bases (for Ga1 and Ga2), and a cube Er_8 (for Ga3). The partial replacement of Ga atoms by Ti atoms takes place in the site surrounded by an Er_8 cube, which has larger volume than the Er_8 square antiprisms.

In the structure of $Y_{2.97(1)}Ti_{0.08(2)}Ga_{1.95(1)}$ the partial replacement of Y atoms by Ti atoms takes place in the site with lower coordination number, *i.e.* the site surrounded by a Ga_6Er_6 icosahedron.

Conclusions

In the ternary systems {Y, Er}–Ti–Ga at 500 and 600ºC substitutional solid solutions of Ti in the binary compounds Y_3Ga_2 and Er_3Ga_2 are formed. In the case of Y_3Ga_2 the titanium atoms substitute for both Y and Ga atoms ($Y_{3-x}Ti_{x+y}Ga_{2-y}$), whereas in Er_3Ga_2 the titanium atoms exclusively replace Ga atoms ($Er_3Ti_yGa_{2-y}$). Substitution takes place in selected sites, which is in agreement with the atom radii.

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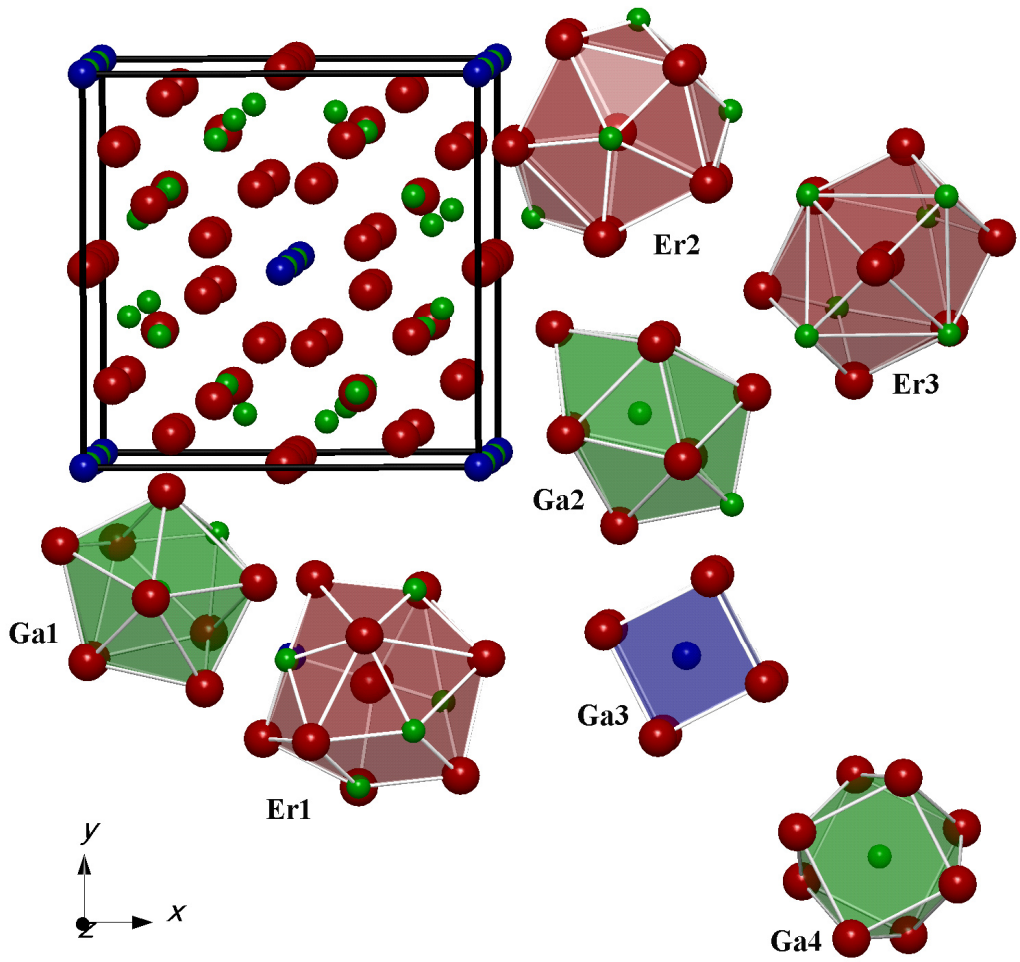

Fig. 3 Unit cell content and coordination polyhedra in the structure of $Er_3Ti_{0.08(2)}Ga_{1.92(2)}$.

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