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Ternary intermetallic RAgGa, RAuGa alloys (R=light rare earth and Yb)

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Abstract

Ternary alloys of light rare earths and Yb with silver and gallium, gold and gallium, on 1:1:1 stoichiometric ratio, were synthesised and structurally determined. New phases were identified for R=La, Ce, Pr, Nd, Sm, Yb. The crystal structures of alloys were found to be related to the orthorhombic *oI*12–$CeCu_2$ (=KHg_2) type. The $PrAg_{2-x}Ga_x$ and $PrAu_{2-x}Ga_x$ sections ($0\leq x\leq 2$) were also analysed. The stability range of the observed *oI*12–$CeCu_2$ and *hP*3–AlB_2 type structures were determined.

Keywords: *hP*6–$CaIn_2$ type compounds; Rare earth ternary alloys; Rare earth gold gallides; Rare earth silver gallides

1. Introduction

Recently, during a systematic study concerning the existence and the crystal structure of new ternary intermetallic phases formed by rare earth metals (R) with transition metals (T) and elements (X) of the 13th, 14th, 15th groups of the periodic Table, we have analysed ternary $RAg_{0.5}Ga_{1.5}$ and $RAu_{0.5}Ga_{1.5}$ alloys and some $RAg_{2-x}Ga_x$ and $RAu_{2-x}Ga_x$ sections ($1\leq x\leq 2$). Several phases pertaining to these sections, having the *oI*12–$CeCu_2$, *hP*6–$CaIn_2$ or *hP*3–AlB_2 type structures, have been synthesised and characterised [1,2]. Following these two papers, we have now examined some intermetallic 1:1:1 phases formed by light rare earths and ytterbium with silver and gallium, gold and gallium. The RAgGa, RAuGa compounds with heavy rare earths were already studied by Dwight [3,4]. The trends of the average atomic volumes of the 1:1:1 and 1:0.5:1.5 alloys have been examined and discussed. Some samples moreover in the $PrAg_2$–$PrGa_2$ and $PrAu_2$–$PrGa_2$ sections have also been synthesised and analysed. The behaviour of praseodymium, different from that shown by Gd in the analogous systems [1,2], may be related to a different value of the dimensional ratio of the atoms involved.

2. Experimental details

The experimental investigation was carried out by using conventional preparative and analytical techniques: X-ray diffraction analysis, metallographic analysis and electron probe microanalysis. The metals used had a nominal purity of 99.9 mass% for the rare earth, 99.99 mass% for gold, silver and gallium. The alloys were prepared by sealing the appropriate amounts of the metals (1–1.2 g each sample) in small tantalum crucibles under an argon atmosphere. The crucibles were induction-heated, until complete fusion of the constituent elements, in a vacuum-tube furnace. The alloys were homogenised by repeated shaking and quickly cooled to room temperature. The samples were then annealed at 500°C for 1 week and quenched in cold water. Optical and electronic metallographic examination was carried out on all samples after etching in a dilute solution of HNO_3 (0.5–0.2 vol.%) in the case of Ag alloys, and in a dilute solution of HNO_3 and HCl (1:5) in the case of Au alloys. For a semi-quantitative microanalysis of the phases an energy-dispersive X-ray microanalyzer was used with pure elements as standard. The crystal structures of the phases and their lattice parameters were determined by using the Debye–Scherrer method on powder samples with Fe–Ka filtered radiation. The values of the lattice parameters were computed and refined through a least-squares interpolation, the values of *d* being corrected by applying the Nelson–Riley function. The observed diffraction intensities of the isotypic compounds were compared with the values calculated by the LAZY PULVERIX program [5].

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3. Results

3.1. RAgGa and RAuGa alloys

Twelve new RAgGa, RAuGa phases were synthesized and structurally determined in the systems with R=La, Ce, Pr, Nd, Sm, Yb. Micrographic and microprobe analysis showed the samples to be homogeneous and to have a composition very close to the nominal one. From the X-ray analysis the phases were found to be isostructural with the analogous compounds formed with the heavy rare earths already known in literature [3,4]. The powder photographs of the phases were indexed on the basis of an orthorhombic cell. A fair agreement was observed between the experimental diffraction pattern intensities and those computed on the basis of the following atomic positions in the *oI*12–$CeCu_2$ (=KHg_2) type structure (space group *Imma*): 4R in 4*e* (0, 1/4, z_1), 4T and 4Ga in 8*h* (0, *y*, z_2) with $z_2 \cong 0.166$, z_1 ranging between 0.53 and 0.54 and *y* between 0.044 and 0.052 (the lower values are in better agreement with the data of light rare earths, the higher ones with the data of Yb). The data obtained in the present work are reported and compared with those of the literature in Tables 1 and 2.

3.2. $PrAg_{2-x}Ga_x$ and $PrAu_{2-x}Ga_x$ sections

The Pr–Ag–Ga and Pr–Au–Ga systems have been investigated along the $PrAg_{2-x}Ga_x$ and $PrAu_{2-x}Ga_x$ sections ($0 \leq x \leq 2$) in the region included between PrT_2 ($CeCu_2$ type phase) and $PrGa_2$ (AlB_2 type phase). The results are reported in Tables 3 and 4. In these sections only phases with the orthorhombic *oI*12–$CeCu_2$ type (Ag or Au rich alloys) or the hexagonal *hP*3–AlB_2 type (Ga rich alloys) structures have been observed. The *oI*12–$CeCu_2$ type structure is stable from $x=0$ to $x \cong 1.3$–1.4. For *x*, approximately included between 1.5 and 1.6, two-phase alloys have been obtained.

4. General remarks

In Fig. 1 the trends of the average atomic volumes of RAgGa, RAuGa are reported in function of the atomic number of the rare earth. Moreover the data concerning the $RAg_{0.5}Ga_{1.5}$ and $RAu_{0.5}Ga_{1.5}$ alloys [1,2] are reported for a comparison. We may note the typical behaviour of Yb, which (as Eu) deviates from the trend of the 'trivalent' rare earths.

Generally the Au-alloys have smaller volumes than Ag-alloys (notice also the higher volume contractions, characteristic of the Au alloys). Notice, moreover, that, on passing from the 1:1:1 phases to the 1:0.5:1.5 alloys, the substitution of Ga to Ag or Au, increases the volumes of the R–Au–Ga alloys, while it reduces those of the R–Ag–Ga phases, even if the Ga atomic volume is larger than those of Ag and Au. This could possibly be related to a variation in the average bond energy. For lack of experimental data, reference to this point could possibly be given by the trend of the computed (according to Miedema) formation enthalpies. For the 1:1 RMe compounds following the values have been reported (KJ/mol at.) for R=La or Y: 108–110 (Me=Au), 74–73 (Me=Ga) and 43–44 (Me=Ag) [10].

Table 1
Crystal data for ternary orthorhombic RAgGa alloys (*oI*12 $CeCu_2$ type)

Phase	Lattice parameters (pm)			Axial ratio		$\bar{V}$ [a] ($pm^3 * 10^{-6}$)	$\Delta V/V$ [b] (%)	Ref. [c]
	a	*b*	*c*	*b/a*	*c/a*			
LaAgGa	469.7	754.0	794.9	1.605	1.692	23.5	−4.9	t.w.
CeAgGa	465.8	744.3	791.8	1.598	1.700	22.9	−3.5	t.w.
PrAgGa	463.1	740.8	788.4	1.600	1.702	22.5	−5.0	t.w.
NdAgGa	462.4	732.3	787.8	1.584	1.704	22.2	−5.9	t.w.
SmAgGa	458.1	722.5	783.8	1.577	1.711	21.6	−7.1	t.w.
EuAgGa	470.2	757.8	794.5	1.612	1.690	23.6	−16.5	[4]
GdAgGa	456.9	715.3	781.9	1.566	1.711	21.3	−8.3	[3]
GdAgGa	456.6	715.2	783.3	1.566	1.715	21.3	−8.2	[1]
TbAgGa	454.2	711.9	779.6	1.567	1.716	21.0	−8.3	[3]
DyAgGa	452.1	705.4	779.8	1.560	1.725	20.7	−9.0	[3]
HoAgGa	452.6	700.1	780.2	1.547	1.724	20.6	−8.9	[3]
ErAgGa	449.6	698.1	777.6	1.553	1.730	20.3	−9.5	[3]
TmAgGa	449.2	691.4	778.2	1.539	1.732	20.1	−9.7	[3]
TmAgGa	448.3	693.4	778.5	1.547	1.737	20.2	−9.6	[1]
YbAgGa	459.9	722.7	785.1	1.571	1.707	21.8	−16.2	t.w.
LuAgGa	448.8	686.0	776.2	1.529	1.730	19.9	−9.8	[3]
YAgGa	452.6	706.6	780.4	1.561	1.724	20.8	−10.9	[3]

[a] Average atomic volume $\bar{V} = V_{cell}/12$.

[b] Volume contraction values, $\Delta V/V(\%) = 100 * (V_{cell} - \Sigma V_{at})/\Sigma V_{at}$, the atomic volumes of elements (V_{at}) are from Ref. [5].

[c] t.w. = this work.

Table 2
Crystal data for ternary orthorhombic RAuGa alloys (*oI*12 $CeCu_2$ type)

Phase	Lattice parameters (pm)			Axial ratio		$\bar{V}$[a] (pm^3*10^{-6})	$\Delta V/V$[b] (%)	Ref.[c]
	a	*b*	*c*	*b*/*a*	*c*/*a*			
LaAuGa	462.6	752.4	788.2	1.626	1.704	22.9	−7.2	t.w.
CeAuGa	459.5	742.0	788.1	1.615	1.715	22.4	−5.3	t.w.
PrAuGa	457.1	736.1	783.7	1.610	1.715	22.0	−7.3	t.w.
NdAuGa	455.3	731.5	780.4	1.607	1.714	21.7	−8.2	t.w.
SmAuGa	452.5	722.9	777.9	1.598	1.719	21.2	−8.7	t..w
EuAuGa	460.3	756.8	783.8	1.644	1.703	22.8	−19.3	[4]
GdAuGa	450.2	716.1	773.3	1.591	1.718	20.8	−10.4	[3]
TbAuGa	449.3	710.4	771.9	1.581	1.718	20.5	−10.2	[3]
DyAuGa	446.9	708.3	769.3	1.585	1.721	20.3	−10.8	[3]
HoAuGa	446.6	703.6	768.3	1.575	1.720	20.1	−10.8	[3]
ErAuGa	445.5	699.5	767.7	1.570	1.723	20.0	−11.1	[3]
TmAuGa	444.0	695.4	767.8	1.566	1.729	19.8	−11.3	[3]
YbAuGa	449.5	711.3	770.4	1.582	1.714	20.5	−20.8	t.w.
LuAuGa	444.1	688.5	765.6	1.550	1.724	19.5	−11.5	[3]
YAuGa	447.4	707.5	772.1	1.581	1.726	20.4	−12.6	[3]

[a] Average atomic volume $\bar{V}=V_{cell}/12$.

[b] Volume contraction values, $\Delta V/V(\%)=100*(V_{cell}-\Sigma V_{at})/\Sigma V_{at}$, the atomic volumes of elements (V_{at}) are from Ref. [5].

[c] t.w. = this work.

Table 3
Solid phases in the $PrAg_2$–$PrGa_2$ system

$PrAg_{2-x}Ga_x$ Nominal composition	Pearson symbol/ prototype	Lattice parameters (pm)			Axial ratio		$\bar{V}$[a] (pm^3*10^{-6})	Ref.[b]
		a	*b*	*c*	*b*/*a*	*c*/*a*		
$PrAg_2$	*oI*12 $CeCu_2$	478.1	708.4	819.6	1.482	1.714	23.1	[6]
$PrAg_{1.5}Ga_{05}$	*oI*12 $CeCu_2$	470.1	726.4	802.0	1.545	1.706	22.8	t.w.
PrAgGa	*oI*12 $CeCu_2$	463.1	740.8	788.4	1.600	1.702	22.5	t.w.
$PrAg_{0.8}Ga_{1.2}$	*oI*12 $CeCu_2$	460.6	743.6	783.3	1.614	1.701	22.4	t.w.
$PrAg_{0.5}Ga_{1.5}$[c]	*oI*12 $CeCu_2$	459.2	743.4	781.8	1.619	1.703	22.2	t.w.
	*hP*3 AlB_2	427.8		428.2		1.001	22.6	t.w.
$PrGa_2$	*hP*3 AlB_2	428.0		428.6		1.001	22.7	[7]

[a] Average atomic volume: $\bar{V}=V_{cell}/12$ for $CeCu_2$ structure type, $V_{cell}/3$ for AlB_2 structure type.

[b] t.w. = this work.

[c] Two phases sample.

Table 4
Solid phases in the $PrAu_2$–$PrGa_2$ system

$PrAu_{2-x}Ga_x$ Nominal composition	Pearson symbol/ prototype	Lattice parameters (pm)			Axial ratio		$\bar{V}$[a] (pm^3*10^{-6})	Ref.[b]
		a	*b*	*c*	*b*/*a*	*c*/*a*		
$PrAu_2$	*oI*12 $CeCu_2$	467.2	704.0	817.8	1.507	1.750	22.4	[8]
$PrAu_2$	*oI*12 $CeCu_2$	467.5	703.9	813.6	1.548	1.724	22.3	[9]
$PrAu_{1.5}Ga_{0.5}$	*oI*12 $CeCu_2$	462.9	718.8	797.7	1.553	1.723	22.1	t.w.
PrAuGa	*oI*12 $CeCu_2$	457.1	736.1	783.7	1.610	1.715	22.0	t.w.
$PrAu_{0.8}Ga_{1.2}$	*oI*12 $CeCu_2$	456.0	742.0	778.0	1.627	1.706	21.9	t.w.
$PrAu_{0.5}Ga_{1.5}$[c]	*oI*12 $CeCu_2$	455.2	745.1	774.6	1.637	1.702	21.9	t.w.
	*hP*3AlB_2	428		428		1.000	22.7	t.w.
$PrAu_{0.4}Ga_{1.6}$[c]	*oI*12 $CeCu_2$	456.1	745.8	774.4	1.698	1.698	22.0	t.w.
	*hP*3 AlB_2	428.4		427.3		0.997	22.6	t.w.
$PrGa_2$	*hP*3 AlB_2	428.0		428.6		1.001	22.7	[7]

[a] Average atomic volume: $\bar{V}=V_{cell}/12$ for $CeCu_2$ structure type, $V_{cell}/3$ for AlB_2 structure type.

[b] t.w. = this work.

[c] Two phases sample.

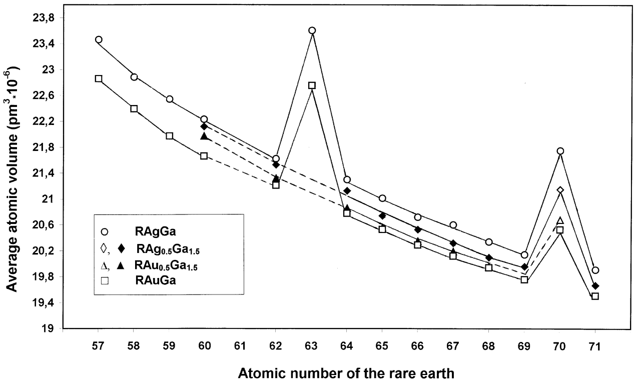

Fig. 1. Average atomic volume plotted as a function of the atomic number of the rare earth for the phases RAgGa (○), RAuGa (□), $RAg_{0.5}Ga_{1.5}$ (◇, ♦), $RAu_{0.5}Ga_{1.5}$ (△, ▲). Filled symbols are used for the hexagonal *hP*6–$CaIn_2$ type structure, the empty ones for the orthorhombic *oI*12–$CeCu_2$ type structure.

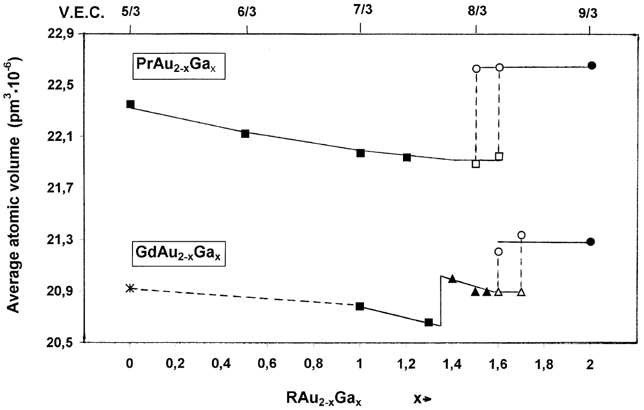

Fig. 3. Average atomic volume plotted as a function of the nominal composition of samples $PrAu_{2-x}Ga_x$ and $GdAu_{2-x}Ga_x$, in the range ($0 \leq x \leq 2$). Structures: *oI*12–$CeCu_2$ type (□, ■); *hP*3–AlB_2 type (○, ●); *hP*6–$CaIn_2$ type (△, ▲); *tI*6–$MoSi_2$ type (*). Filled symbols are used for homogenous samples, the empty ones for two phase samples.

In Figs. 2 and 3 the trend of the average atomic volumes along the $PrAg_{2-x}Ga_x$ and $PrAu_{2-x}Ga_x$ sections are reported in function of the nominal composition of the samples (and compared with that of Gd alloys). We may note that the hexagonal *hP*6–$CaIn_2$ type structure, previously observed with Gd in the $RAg_{2-x}Ga_x$, $RAu_{2-x}Ga_x$ systems for composition close to 1:0.5:1.5 [1,2], is not formed by praseodymium. This fact may be due to effects related to the dimensional ratio of the atoms involved. It was already observed in several $RT_{2-x}X_x$ sections [11] that, on passing from one R to another with the same T and X metals, the stability field of the *hP*6–$CaIn_2$ type structure decreases, by increasing the R radius. Moreover, in previous works [1,2,12], we have remarked that the *oI*12–$CeCu_2$ type structure changes in the $CaIn_2$ type when, for a valence electron concentration (v.e.c.) near to 2.6, the axial ratio c/a of orthorhombic phases, on increasing the x value, becomes close to 1.73 ($=\sqrt{3}$). In the case of $PrAg_{2-x}Ga_x$ and $PrAu_{2-x}Ga_x$ sections, when, on increasing the x value, the v.e.c. becomes close to 2.6, the c/a ratio is smaller than the $\sqrt{3}$ limit value.

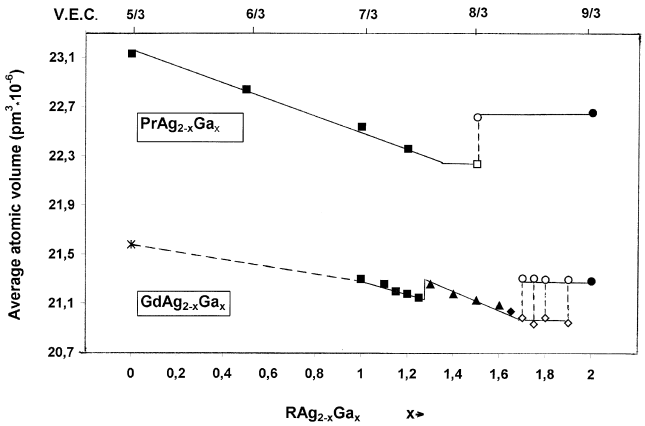

Fig. 2. Average atomic volume plotted as a function of the nominal composition of samples $PrAg_{2-x}Ga_x$ and $GdAg_{2-x}Ga_x$, in the range ($0 \leq x \leq 2$). Structures: *oI*12–$CeCu_2$ type (□, ■); *hP*3–AlB_2 type (○, ●); *hP*6–$CaIn_2$ type (▲); *hP*3–$CeCd_2$ type (◇, ♦); *tI*6–$MoSi_2$ type (*). Filled symbols are used for homogenous samples, the empty ones for two phase samples.

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