Crystal structure of mono(silver, gallium) trimagnesium, $Ag_{0.55}Ga_{0.45}Mg_3$

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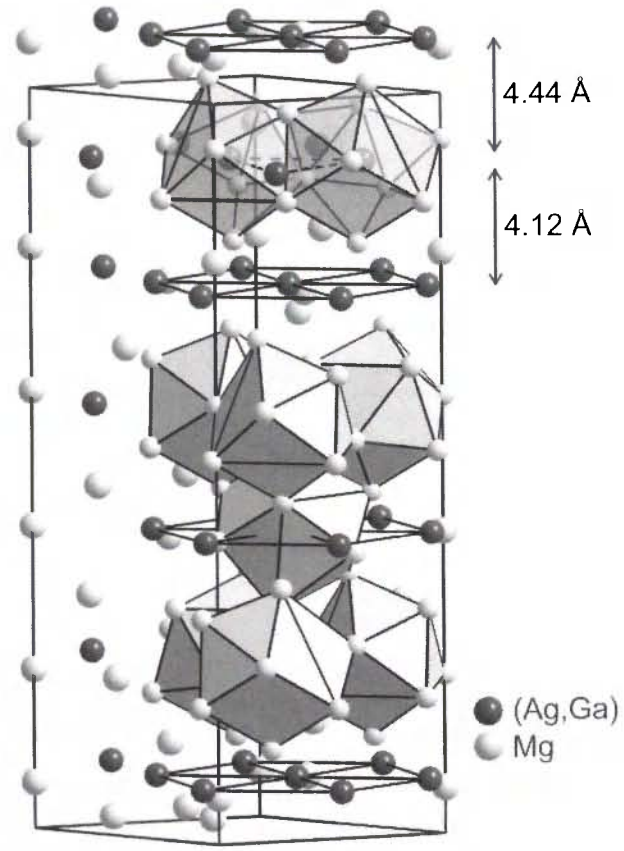

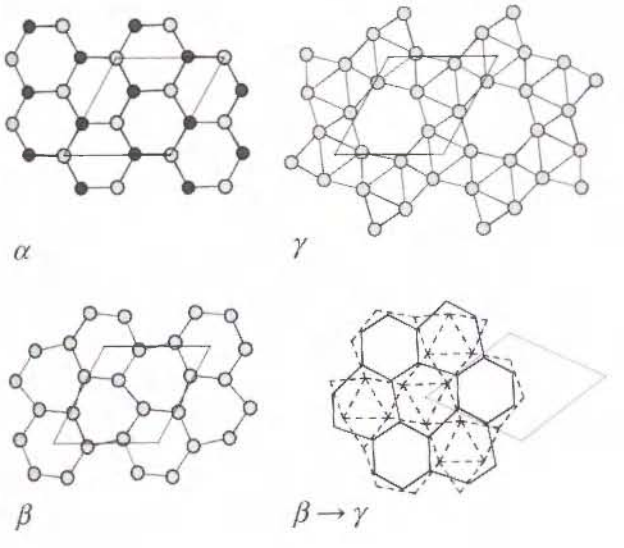

Abstract

$Ag_{0.55}Ga_{0.45}Mg_3$, trigonal, $R\bar{3}$ (no. 148), a = 8.248(1) Å, c = 25.658(4) A, V = 1511.8 Å^3, Z = 18, $R_{gt}(F)$ = 0.031, $wR_{ref}(F^2)$ = 0.060, T = 293 K.

Source of material

Single crystals of the title compound with metallic lustre were obtained from a sample of the nominal composition $Ag_{9.6}Ga_{16.0}Mg_{74.4}$ containing Mg and Mg_5Ga_2 as additional phases. Several alloys were prepared by melting mixtures of the elements (Ag, 99.995 %; Ga, 99.999 %; Mg, 99.98 %) in weld-sealed tantalum ampoules which were encapsulated in silica envelopes for the heat treatment of 96 hours at 623(5) K. Finally, the samples were quenched in water.

Chemical analyses on impurities of O, N, C and H were carried out using the carrier gas hot extraction or the combustion technique. All impurities were below the respective limit of detection: O < 500 ppm, N < 100 ppm, C < 600 ppm, H < 30 ppm. The number of phases and their composition have been obtained from a microscopic examination in combination with EDXS analysis ($Ag_{13.5}Ga_{10.3}Mg_{76.2}$) of the microstructure.

Experimental details

The unit cell parameters were determined from least-squares fittings of 23 reflections taken from a Guinier powder pattern (Huber G670, Ge monochromator, CuKα_1 radiation, λ = 1.5405929 Å, Si powder SRM 640c as internal standard, a = 5.431195(9) Å).

Discussion

Intermetallic compounds of the general formula MMg$_3$ with M = Ir, Pt and Au [1,2] adopt the Cu_3P structure type (Z = 6, $P6_3cm$). Cu_3P and the closely related structure types of Na_3As (Z = 2, $P6_3/mmc$) and LaF_3 (Z = 6, $P\bar{3}c1$) are space-filling arrangements of filled Edshammar polyhedra (CN 11), i.e. full-capped trigonal prisms, and empty cubes [3]. The Edshammar polyhedra form close-packed layers which alternate with layers of cubes along [001]. The respective unit cell and symmetry depend on the distortion of the Edshammar polyhedra. For $HgMg_3$ [4] a rhombohedral stacking variant of the Cu_3P structure type has been proposed (Z = 18, $R32$) whereas a recent re-determination of the Ag-Mg system [5-7] rules out the existence of an Edshammar phase $AgMg_3$. However, in the Ag-Ga-Mg system the phase $Ag_xGa_{1-x}Mg_3$ forms with $x \approx 0.55$ and a valence electron concentration close to that of $HgMg_3$.

In the rhombohedral structure of $Ag_{0.55}Ga_{0.45}Mg_3$ all Ag and Ga atoms randomly occupy one crystallographic 18f site. They are enclosed by ten Mg atoms forming a distorted polarly bicapped square antiprism (d((Ag,Ga)—Mg) = 2.78 Å – 3.19 Å). Mg4 is coordinated icosahedrally whereas the remaining Mg atoms exhibit irregular coordination with 12 to 14 neighbors

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(d(Mg—Mg) = 2.97 Å – 3.73 Å). The (Ag,Ga) positions form a distorted *hcp* arrangement (d((Ag,Ga)—(Ag,Ga)) = 4.62 Å – 4.96 Å) with six 3^6 layers per unit cell along [001]. Hence, the antiprisms form hexagonal close-packed layers stacked along [001] (figure, top). The remaining space is filled by alternating layers of empty Mg_8 cubes and layers of empty Mg_8 cubes and Mg_4 tetrahedra depending on the 3^6 inter-layer distance of 4.12 Å and 4.44 Å, respectively.

A convenient way to describe the Cu_3P structure type is to separate the atoms into puckered layers. The stacking is characterized by the sequence $|\alpha\beta\alpha^*\beta|$ per unit cell with α and β denoting two different kinds of puckered layers and α^* related to α by a 6_3 symmetry operation: α – 6^3 layer of (Ag,Ga) and Mg, β – 6^3 layer of Mg. In case of $Ag_{0.55}Ga_{0.45}Mg_3$ a triple hexagonal cell is found with the following layer sequence: $|\{\alpha\beta\alpha^*\gamma\}\{\alpha\beta\alpha^*\gamma\}'\{\alpha\beta\alpha^*\gamma\}''|$ (figure, bottom). Here α and α^* are related by inversion while prime and double prime denote R-centring translation. γ is a puckered $3^4.6$ Mg layer. The relationship of the title compound to the Cu_3P structure type is illustrated by transforming the β layer into the γ layer by a correlated displacement of all Mg atoms by about 1 Å in the layer. This corresponds with a removal of one Mg atom per Edshammar polyhedron. After a slight relaxation of the remaining atoms the polarly bi-capped square antiprism is obtained. For a discussion of the relationship between $HgMg_3$ and the title compound as well as the influence of the valence electron concentration a re-evaluation of the crystal structure of $HgMg_3$ and detailed investigations of the homogeneity ranges have to be done.

Table 1. Data collection and handling.

Crystal:	silver, irregular, size 0.025 × 0.060 × 0.120 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	72.55 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC7 & Mercury CCD, ω/φ
$2\theta_{max}$:	63.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4366, 1157
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1072
$N(param)_{refined}$:	38
Programs:	SHELXL-97 [8], DIAMOND [9]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	18*f*	0.545(9)	0.00375(3)	0.32566(3)	0.246871(8)	0.0167(1)	0.0135(1)	0.0149(1)	0.0063(1)	0.00041(7)	0.00103(7)
Ga(1)	18*f*	0.455	0.00375	0.32566	0.246871	0.0167	0.0135	0.0149	0.0063	0.00041	0.00103
Mg(1)	18*f*		0.0237(1)	0.3175(2)	0.13653(4)	0.0212(5)	0.0303(6)	0.0173(4)	0.0157(5)	0.0017(4)	0.0019(4)
Mg(2)	18*f*		0.4074(2)	0.1006(2)	0.02158(4)	0.0281(6)	0.0272(6)	0.0195(4)	0.0178(5)	0.0008(4)	–0.0040(4)
Mg(3)	6*c*		0	0	0.06275(8)	0.0166(5)	U_{11}	0.037(1)	½U_{11}	0	0
Mg(4)	6*c*		0	0	0.21454(7)	0.0143(5)	U_{11}	0.0327(9)	½U_{11}	0	0
Mg(5)	6*c*		0	0	0.40894(7)	0.0146(5)	U_{11}	0.0327(9)	½U_{11}	0	0

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