

Synthesis and crystal structure refinement of cubic $\text{Mg}_{6.8}\text{Y}$

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Abstract

The crystal structure of the Mg-rich compound in the Mg–Y system was determined on a single crystal. Refinement showed its composition to be $\text{Mg}_{6.8}\text{Y}$. The crystal structure is a variant of the cubic α -Mn-type (space group $I\bar{4}3m$). In contradistinction to a previous structure report we found that the 8c site shows mixed occupancy, whereas the 2a site is exclusively occupied by Y.

Keywords: Intermetallic compound; Crystal structure; Mg–Y compound

1. Introduction

The magnesium–yttrium phase diagram [1] contains three intermetallic compounds: MgY, Mg_2Y , and a phase called Mg_{24}Y_5 . The latter forms peritectically and crystallizes with a substitution variant of the cubic α -Mn-type structure (space group $I\bar{4}3m$, Pearson code cI58). The composition Mg_{24}Y_5 (82.8 at.% Mg) refers to a fully ordered structure in which magnesium occupies two 24g sites, and yttrium the 8c and 2a sites. The true structure, however, is partly disordered and the composition Mg_{24}Y_5 is outside the experimentally determined homogeneity range which extends from about 84 to 87 at.% Mg at 525°C [2].

A single-crystal X-ray structure refinement [2] at the magnesium-poor phase limit suggested that the site 2a has mixed occupancy, corresponding to the composition 83.6 at.% Mg. However, estimated standard deviations and agreement indices were not given. Apart from that study, no other single-crystal structure refinements on this compound or other magnesium-rich intermetallics having similar structures and atomic ratios have appeared in the literature [3]. We therefore decided to carry out an X-ray investigation on an Mg_{24}Y_5 crystal at the magnesium-rich phase limit.

2. Experimental

A sample was synthesized from the elements at the nominal composition 88 at.% Mg and 12 at.% Y by

induction melting in an alumina crucible under an argon pressure of 4 bar in order to prevent evaporation. It was annealed at 525°C for 2 weeks in a sealed quartz tube. X-ray powder diffraction confirmed the presence of the cubic α -Mn-type phase with a refined cell parameter of $a = 11.2507(2)$ Å. Optical micrography showed the presence of about 5 vol.% secondary phase which was not seen on the X-ray pattern. Microprobe analysis (EDAX) indicated that the composition of the main phase was 87(2) at.% Mg and 13(2) at.% Y, and that the secondary phase was a solid solution of approximate composition 96 at.% Mg and 4 at.% Y. The composition and cell parameter of the main phase are consistent with those reported for the magnesium-rich boundary of the Mg_{24}Y_5 phase [2].

A single crystal of irregular shape (mean diameter of about 80 μm) suitable for X-ray diffraction analysis was selected from the crushed alloy and mounted on a Philips PW1100 automatic four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator). During the first stages of structure refinement the intensities of the Friedel pairs were not merged, yielding an absolute structure parameter which suggested that the set of positional parameters chosen was the correct one. Only one atom site, e.g. 8c, was found to have mixed occupancy (Y/Mg ~ 2). No evidence for mixed or partial occupancy was found for the other sites (error limits about 1%), in particular for site 2a, which was previously identified [2] as a mixed atom site. Thus their population parameters were fixed at unity,

and the sum of the occupancies of the mixed atom site 8c was constrained to 100%. The refined composition of that model, $Mg_{6.8}Y$ (87.2 at.% Mg, 12.8 at.% Y), was in good agreement with the results of the microprobe analysis. The parameters of data collection and structure refinement are given in Table 1. All calculations were performed with the XTAL3.2 system [4]. The structural results are summarized in Table 2 and the interatomic distances in Table 3.

As expected, our refinement results differ significantly from those reported previously [2]. In the presently investigated magnesium-rich crystal the 8c site shows mixed occupancy and the 2a site is occupied by yttrium only, whereas in the previously investigated magnesium-poor crystal the 2a site shows mixed occupancy and the 8c site is occupied by yttrium only. Notice that a hypothetical substitution of yttrium by magnesium on site 2a only would account for a compositional range ($Mg_{4.8}Y$ – $Mg_{6.25}Y$) which is outside the observed magnesium-rich phase limit ($Mg_{6.8}Y$). It is therefore not surprising that the 8c site in our magnesium-rich crystal shows mixed occupancy. What is surprising, however, is the fact that in this crystal all excess magnesium (with respect to the ideal composition $Mg_{24}Y_5$) goes on that site at the expense of site 2a which shows mixed occupancy in the magnesium-poor crystal. In view of this unusual behaviour, and considering the absence of error estimates in the previous structure work [2], a re-investigation of the

Table 1
Data collection and refinement parameters

($\sin \theta/\lambda$) range (\AA^{-1})	0.089–0.725
hkl range	$-16 \leq h \leq 16$ $-11 \leq k \leq 11$ $-11 \leq l \leq 16$
Collected reflections	1044
Independent reflections	261
Linear absorption coefficient (mm^{-1})	7.9
R_{int}	8.98
Number of reflections with $I_{rel} > 1.5 \sigma(I_{rel})$	200
Number of parameters	18
Final residual electron density (\AA^{-3})	1.7 –3.1
Goodness of fit	1.43
$R(F)$ (%)	6.35
$R_w(F)$, $w = 1/\sigma^2(F_{rel})$ (%)	4.42

Table 2
Refined structural parameters for $Mg_{6.8}Y$

Atom	Site	x	y	z	$U_{eq}(10^{-2} \text{\AA}^2)$	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Y	2a	0	0	0	0.97(5)	0.97(9)	U_{11}	U_{11}	0	0	0
M	8c	0.3136(1)	x	x	1.37(4)	1.37(7)	U_{11}	U_{11}	0.20(6)	U_{12}	U_{12}
Mg1	24g	0.3576(2)	x	0.0357(3)	2.1(1)	2.4(2)	U_{11}	1.5(2)	–0.1(2)	0.6(1)	U_{13}
Mg2	24g	0.0905(2)	x	0.2807(3)	1.8(1)	1.9(1)	U_{11}	1.7(2)	–0.7(2)	–0.33(9)	U_{13}

$M = 0.679(9)Y + 0.321(-) Mg \Rightarrow$ refined composition: $Mg_{6.80(7)}Y$. Space group $I \bar{4} 3 m$ (no. 217); Pearson code cI58. $a = 11.2507(2) \text{\AA}$, $V = 1424.09(8) \text{\AA}^3$, $D_x = 2.2 \text{ g cm}^{-3}$.

Table 3
Interatomic distances shorter than 4 \AA

Y	–12 Mg2	3.470(3)	M	–3 Mg1	3.203(3)
	–4 M	3.633(1)		–6 Mg2	3.463(3)
				–3 Mg2	3.569(3)
Mg1	–Mg2	2.986(5)		–Y	3.633(1)
	–2 Mg2	3.188(4)		–3 Mg1	3.697(3)
	–M	3.203(3)			
	–2 Mg1	3.302(3)	Mg2	–Mg2	2.878(4)
	–4 Mg1	3.365(3)		–Mg1	2.986(4)
	–2 Mg2	3.386(4)		–2 Mg2	3.027(4)
	–M	3.697(3)		–2 Mg1	3.188(3)
				–2 Mg1	3.386(4)
				–2 M	3.463(3)
				–Y	3.470(3)
				–M	3.569(3)

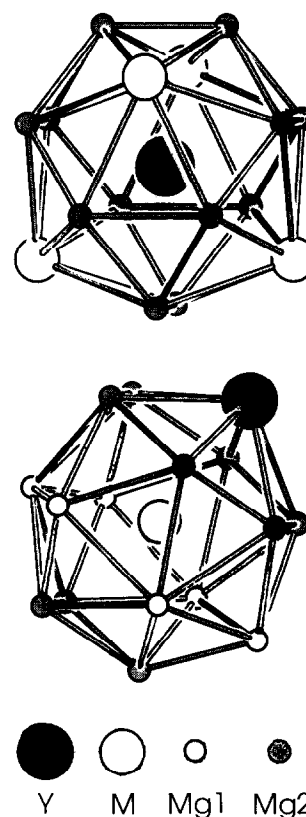


Fig. 1. Coordination polyhedron of Y (top) and of the mixed site M (bottom).

atom distribution in magnesium-poor crystals is desirable.

Finally, it is worth pointing out that the two sites occupied by yttrium have very similar atom coordinations which can be described as 16-vertex Frank–Kasper polyhedra (see Fig. 1). The average bond distances involving these sites are 3.51 Å (Y on 2a) and 3.49 Å (M on 8c). No M–M contacts (M: mixed site) are present in the structure.

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