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Crystal structure of κ-Ag₂Mg₅ Facundo J. Castro^{1 a, b}, Gastón A. Primo^c, Guillermina Urretavizcaya^{a, b}

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Abstract

The structure of κ -Ag₂Mg₅ has been refined based on X-ray powder diffraction measurements (R_{wp}) = 0.083). The compound has been prepared by combining mechanical alloying techniques and thermal treatments. The intermetallic presents the prototypical structure of Co₂Al₅, an hexagonal crystal with the symmetries of space group $P6_3/mmc$, and belongs to the family of kappa-phase structure compounds. The unit cell dimensions are a=8.630(1) Å and c=8.914(1) Å. Five crystallographically independent sites are occupied, Wyckoff positions 12k, 6h and 2a are filled with Mg, another 6h site is occupied with Ag, and the 2c site presents mixed Ag/Mg occupancy. The crystal chemistry of the structure and bonding are briefly discussed in the paper.

Keywords: Intermetallics, Structure, Crystal chemistry, X-ray diffraction, Mechanical alloying and milling

1 Introduction

The kappa-phase structure compounds constitute a crystallographic family based on the structure of $W_{10}Co_3C_{3,4}$ [1]. These compounds crystallize in the hexagonal system, space group $P6_3/mmc$. The metal atom substructure of this prototypical structure is that of Mn₃Al₁₀, and the different kappa-phase structure compounds are obtained by filling the trigonal prismatic (2c) or the octahedral (6g) interstices of this "host lattice" by p elements or transition metals. If only the trigonal prismatic interstices are filled, the Co₂Al₅ prototypical structure is obtained. On the other hand, if no more than the octahedral interstices are occupied the $Mo_{12}Cu_3Al_{11}C_6$ structure is obtained. Some compounds have both interstices filled [1].

During an experimental study conducted to analyze MgH₂ destabilization by the formation of Ag-Mg alloys we have identified an intermetallic compound denoted for simplicity Ag₂Mg₅ that crystallizes with the Co₂Al₅ structure. Up to now, only eleven compounds with this prototypical structure have been reported [2-3], together with numerous RE₁₀TMCd₃ and RE₁₀TMAl₃ (RE: rareearth metal, TM: transition metal) ternary compounds with anti-Co₂Al₅ structure recently identified [4-5]. Interestingly, four of the Co₂Al₅ structure compounds contain Mg and show some regularity in the periodic table of the elements, namely: Ir₂Mg₅ [6], Rh₂Mg₅ [7], Pd₂Mg₅ [3], and the ternary compound Ir_{2.096}Mg_{1.980}In_{2.924} [3]. The existence of the intermetallic Ag₂Mg₅ follows this trend. To the best of our knowledge this compound has been only previously mentioned in a PhD thesis [8] and is not included in the Ag-Mg equilibrium phase diagrams [9-11]. We present here the refinement of its structure, based on X-ray diffraction experiments on powders.

2 Experimental and refinement details

The compound was prepared by combining mechanical alloying techniques and thermal treatments. A mixture of magnesium and silver with molar ratio Mg:Ag = 5.25:2 was mechanically alloyed in a planetary mill (Fritsch Monomill Pulverisette 6) under pure argon (99.999 %)

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atmosphere during 10 h. The milling conditions were: 0.5 MPa of argon pressure, ball-to-powder mass ratio equal to 40:1, rotational speed of 400 rpm, and steps of 10 minutes of milling followed by 10 minutes of pause. As raw materials Ag nanopowder (< 100 nm, 99.5%, Sigma-Aldrich) and Mg powder obtained from MgH₂ decomposition at 355°C under vacuum were employed. The hydride used to produce Mg was obtained by milling MgH₂ (hydrogen storage degree, Sigma-Aldrich) under hydrogen (99.999 %) during 10 h (similar ball-to-powder mass ratio and milling schedule). The only crystalline phase observed in the as-milled mixture was AgMg (ICDD PDF 65-220) with an approximate composition $Ag_{0.4}Mg_{1.6}$. This composition exceeds the equilibrium range of the intermetallic AgMg [9]. However, is usual to obtain non-equilibrium phases by mechanical milling [12]. After a short thermal treatment of 15h at 350°C under 0.2 MPa of Ar the compound Ag_2Mg_5 was observed together with AgMg of approximate composition $Ag_{0.9}Mg_{1.1}$, very close to the equilibrium composition of AgMg at 350°C, according to the phase diagram. This material was further homogenized by a heat treatment at 300°C under 0.2 MPa of Ar atmosphere for 7 days (the temperature has been chosen taking into account that Ag₂Mg₅ decomposes around 450°C [8]). All the materials handling has been done within an Ar filled glovebox with O₂ and H₂O amounts below 1ppm.

X-ray diffraction was measured with a Bruker D8 Advance instrument equipped with a PSD detector (LynxEye) and using CuK_{α} radiation. An air scatter screen was attached to the instrument to reduce background. The sample was mounted on a low-background Si sample holder. Data were taken in the 20 range 10-140° with a 0.010231° step size and a 9 s collection interval. Rietveld refinement of the data was carried out with FullProf [13] using pseudo-Voigt peak-shape functions including an axial divergence asymmetry correction. Sample vertical displacement and micro-absorption effects have been taken into account during the refinement. As individual atomic displacement coefficients could not be reliably refined, only global coefficients were considered. For Ag₂Mg₅ the starting structural parameters have been taken from Co₂Al₅[2]. 3D visualization of the structure has been done with VESTA [14].

3 Results and discussion

The diffractogram of the homogenized material presents three phases: Ag_2Mg_5 (main phase), AgMg and MgO (Fig. 1). This last phase has been formed by reaction of the sample with gaseous impurities during the thermal treatment. Data have been successfully refined including the above mentioned phases. Tables 1 and 2 summarize the main results.

No. of data/parameters	12708/48				
R _{wp}	0.083				
Phases composition and abundance					
Ag _{1.94} Mg _{5.06}	65 wt.%				
$Ag_{0.93}Mg_{1.07}$	27 wt.%				
MgO	8 wt.%				
Ag ₂ Mg ₅ Crystal data					
Refined composition	5Mg5.055				
Ζ					
Formula weight	g mol ⁻¹				
Crystal system	onal				
Space group	<i>P</i> 6 ₃ / <i>mmc</i> (n° 194)				
a	8.630(1) Å				
С	8.914((1) Å			
Volume	0.5749 nm^3				
ρ_{calc}	3.84 g	cm ⁻³			

Table 1. General results of the refinement and crystal structure data for Ag₂Mg₅.

Atom	Wyckoff	Х	у	Z	Occup (%)
	position				
Mg1	12 <i>k</i>	0.2009(5)	2x	0.0517(4)	100
Ag1	6 <i>h</i>	0.8829(2)	2x	1/4	100
Mg2	6 <i>h</i>	0.538(1)	2x	1/4	100
Ag2/Mg3	2c	1/3	2/3	1/4	89(1)/11(1)
Mg4	2a	0	0	0	100

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Table 2. Atomic coordinates for Ag₂Mg₅.

The refinement of the occupancy resulted in single atom full occupancy of the 12k (Mg1), 6h (Ag1), 6h (Mg2) and 2a (Mg4) sites, and mixed Ag/Mg occupancy of the 2c Wyckoff position. The 12k, 6h and 2a sites constitute the metal substructure of the kappa phase structure, whereas the 2c site is the trigonal interstice that can be filled or not, depending on the nature of the atom [1]. In the Co₂Al₅ structure this site is fully occupied by Co, but mixed occupancy of this interstice has been observed in Pd₂Mg₅ [8].

The coordination polyhedra of the Ag and Mg sites are shown in Fig. 2. The atomic environment of Mg1 is an irregular 14-vertex polyhedron Ag₄Mg₁₀, Ag1 is surrounded by a slightly distorted icosahedron Ag₂Mg₁₀, the coordination polyhedron of Mg2 is a tricapped pentagonal prism Ag₃Mg₁₀, that of the 2*c* Wyckoff position (Ag2/Mg3) is a tricapped trigonal prism formed by 9 Mg atoms, and finally, Mg4 is surrounded by an icosahedron Mg₆Ag₆. The complete structure can be imagined as columns built by stacking Mg4 icosahedra in the [001] direction. These icosahedra share the triangular faces made of Ag1 atoms and are interconnected by the Ag2/Mg3 tricapped trigonal prisms formed by Mg1 and Mg2 atoms (Fig. 3).

Atom	Coord.	Neighbour	Distance (Å)
Mg1	1	Ag2/Mg3	2.654(8)
	1	Ag1	2.967(4)
	1	Mg4	3.038(3)
	2	Mg1	3.141(4)
	2	Ag1	3.154(5)
	2	Mg2	3.217(5)
	2	Mg2	3.323(5)
	2	Mg1	3.429(8)
	1	Mg1	3.535(6)
Ag1	2	Mg2	2.816(9)
	2	Mg4	2.834(1)
	2	Mg1	2.967(4)
	2	Ag1	3.032(3)
	4	Mg1	3.154(5)
Mg2	2	Ag1	2.816(9)
	1	Ag2/Mg3	3.059(5)
	4	Mg1	3.217(5)
	4	Mg1	3.323(5)
	2	Mg2	3.331(1)
Ag2/Mg3	6	Mg1	2.654(8)
	3	Mg2	3.059(5)
Mg4	6	Ag1	2.834(1)
	6	Mg1	3.038(3)

Table 3. Interatomic distances within the first coordination spheres.

The interatomic distances within the first coordination spheres are given in Table 3. In the following we compare these distances with those reported for γ -AgMg₄ [15] and for the isostructural Pd₂Mg₅ [3]. The only Ag–Ag pairs in Ag₂Mg₅ are Ag1–Ag1, with an interatomic distance of 3.032 Å, similar to the Ag–Ag distance of 2.96 Å reported for γ-AgMg₄ and comparable to the Ag–Ag distance of 2.889 Å for fcc Ag. This suggests significant Ag–Ag interactions in Ag₂Mg₅. On the contrary, the Pd–Pd distance of 3.200 Å for Pd₂Mg₅ is considerably greater than Pd–Pd distances in fcc Pd (2.751 Å), indicating weak TM–TM interactions in this compound. Mg– Ag distances in Ag₂Mg₅ are in the range 2.65–3.15 Å, a slightly smaller range than 2.70–3.40 Å reported for γ -AgMg₄. Comparing with Mg–Pd distances in Pd₂Mg₅, 2.60–3.11 Å, the values appear very similar, although Pd is smaller than Ag. Mg–Mg distances in Ag₂Mg₅ extend from 3.04 to 3.54 Å, close to the interatomic distances 3.00–3.70 Å for γ -AgMg₄, and covering a wider range than Mg-Mg distances in Pd₂Mg₅, 2.93-3.25 Å. If we compare these values with the Mg-Mg distance of 3.209 Å in hcp Mg we note that 62% of the Mg–Mg pairs within the first coordination sphere in Ag₂Mg₅ have distances greater than 3.209 Å. On the contrary, only 32% of Mg-Mg pairs exceed this value in Pd₂Mg₅ suggesting that Mg–Mg bonding is not as important in Ag₂Mg₅ as it is in Pd₂Mg₅. Therefore predominant bonding in Ag₂Mg₅ is Ag–Ag and Ag–Mg, whereas in Pd₂Mg₅ is Pd–Mg and Mg–Mg [3].

An interesting consequence of the characteristics of bonding in Ag_2Mg_5 is the greater c/a ratio of this compound compared with that of the isostructural compounds Ir_2Mg_5 , Rh_2Mg_5 and Pd_2Mg_5 (Table 4). The difference is due to the greater *c* lattice parameter of Ag_2Mg_5 . From the geometry of the structure (Figs. 2 and 3) it can be seen that the magnitude of *c* depends on the Ag1–Mg4 and Ag1–Ag1 distances. Longer TM1–Mg4 distances and shorter TM1–TM1 distances contribute to greater *c* lattice parameters. This particular combination takes place in Ag_2Mg_5 (Table 4). TM1-Mg4 distances are in all the cases 7–9% shorter than the sum of the corresponding atomic radii but the greater Ag atomic radius produces a longer Ag1–Mg4 distance. On the other hand, the Ag1-Ag1 distance is shorter than the other TM1-TM1distances and, interestingly, it is only 5% greater than Ag–Ag distance in fcc Ag, whereas Rh1–Rh1 and Pd1–Pd1 distances are 14% and 16% greater TM–TM interaction in Ag_2Mg_5 .

Compound	a (Å)	<i>c</i> (Å)	c/a	TM1-Mg4	TM1-TM1	Ref.
				distance (Å)	distance (Å)	
Ir_2Mg_5	8.601	8.145	0.947	-	-	[6]
Rh ₂ Mg ₅	8.536	8.025	0.940	2.678 (2.949)	3.073 (2.689)	[7]
Pd ₂ Mg ₅	8.671	8.164	0.942	2.753 (2.980)	3.200 (2.751)	[3]
Ag ₂ Mg ₅	8.630	8.914	1.033	2.834 (3.057)	3.032 (2.889)	This work

Table 4. Lattice parameters of Mg-containing Co_2Al_5 -type compounds and TM1–Mg4 and TM1–TM1 distances. The numbers between parentheses are the sum of the atomic radii of the elements, estimated from the fcc (TM) or hcp (Mg) structures of the pure metals.

Concerning the stability of κ -Ag₂Mg₅, complementary experiments suggest that this phase is a stable low-temperature phase of the Ag-Mg system. In a DSC experiment (not shown here) it was observed that κ -Ag₂Mg₅ decomposes into AgMg and ϵ -AgMg₃ around 460°C, but interestingly, if this AgMg and ϵ -AgMg₃ mixture is kept at 250°C under Ar atmosphere for 6 days, κ -Ag₂Mg₅ reappears, indicating that the intermetallic is an equilibrium compound. A similar result was reported by Kudla in his PhD dissertation [8]. Detailed thermodynamic studies of the composition of κ -Ag₂Mg₅ and its stability region in the Ag-Mg phase diagram are currently under way.

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Figure captions

Fig. 1. Observed, calculated and difference X-ray diffraction patterns of the homogenized material.

Fig. 2. Coordination polyhedra of Mg1 (orange sphere labelled 1), Ag1 (grey sphere labelled 1), Mg2 (orange sphere labelled 2), Ag2/Mg3 (bicolour sphere labelled 2/3) and Mg4 (orange sphere labelled 4).

Fig. 3. Two views of the complete structure. In orange the coordination polyhedra of Mg4 and in grey the coordination polyhedra of Ag2/Mg3. Black lines represent the unit cell.



Figure 1. Suggested final size: double column





Figure 2. Suggested final size: double column





Figure 3: suggested final size: single column





Highlights

- The structure of κ -Ag₂Mg₅ is refined based on X-ray powder diffraction data. •
- The compound has the prototypical Co₂Al₅ structure. •
- , un his contractions of the second The intermetallic belongs to the family of kappa-phase structure compounds. •
- Predominant bonding in Ag₂Mg₅ is Ag–Ag and Ag–Mg. •