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Mg and Zn disorder in $Mg_{1.59(1)}Zn_{1.41(1)}Sb_2$

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Single crystals of magnesium zinc diantimony, $Mg_{1.59(1)}Zn_{1.41(1)}Sb_2$, were grown by a reaction of elemental Mg, Zn and Sb in an excess of Zn acting as a flux. The compound crystallizes with the trigonal anti-La_2O_3 type (Pearson code hP5). The structure can be regarded as a substitutional derivative of α-Mg_3Sb_2 by replacing some of the Mg atoms in the tetrahedral postion (site symmetry 3m.) with Zn atoms. The other two atoms in the asymmetric unit also occupy special positions, viz. Mg ($\bar{3}m$.) and Sb (3m.).

Comment

A large number of intermetallic compounds with the anti-La_2O_3 type (also referred to as $CaAl_2Si_2$ type) are known (Villars & Calvert, 1991). The difference between the two is in the cations, which in the $CaAl_2Si_2$ structure are on Wyckoff position 1a, whereas the La^{3+} ion in the La_2O_3 structure is located on one of the sites with symmetry 3m. (Wyckoff position 2d). The majority of the compounds crystallizing with
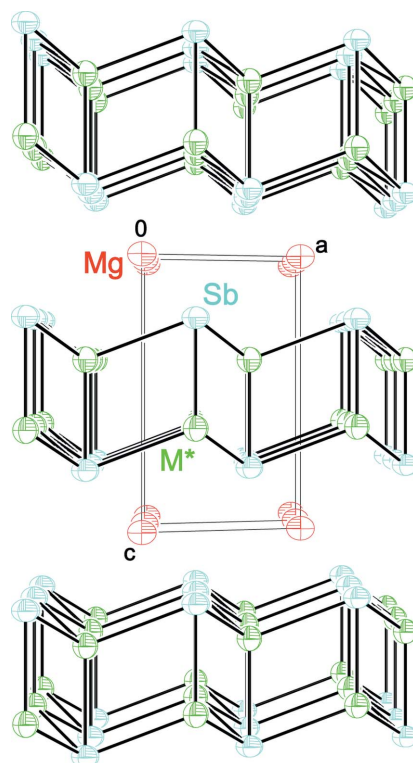

Figure 1
A projection of the crystal structure of $Mg_{1.59(1)}Zn_{1.41(1)}Sb_2$, viewed down the b axis. Displacement ellipsoids are drawn at the 90% probability level. Mg atoms are shown as red, the mixed Zn/Mg atoms (denoted as M*) are shown as green, and the Sb atoms as blue ellipsoids. The unit cell is outlined.

this type are made up of main group elements only, although in recent years many isostructural transition metal phases have also been reported (Cordier & Schäfer, 1976; Zheng & Hoffmann, 1988; Bobev *et al.*, 2006). By means of the extended Hückel method, the formal electron count and the apparent requirement that the CaAl$_2$Si$_2$ type is favored over the rival ThCr$_2$Si$_2$ type for d^0, d^5 and d^{10} configurations has been explained, at least semi-quantitatively (Zheng *et al.*, 1986; Burdett & Miller, 1990).

Fig. 1 shows a perspective view of the layered trigonal crystal structure of Mg$_{1.59 (1)}$Zn$_{1.41 (1)}$Sb$_2$, which can be readily described as double corrugated layers of (Zn,Mg)$_2$Sb$_2{}^{2-}$, separated by Mg^{2+} cations. The corresponding interatomic distances are given in Table 1. The double-layers could be derived by puckering of 'dimerized' graphite-like layers or by splitting of a wurtzite-type framework and a subsequent reconstruction (Burdett & Miller, 1990). Further details on the local and extended bonding in CaAl$_2$Si$_2$-type intermetallics have been given full consideration in earlier publications (Deller & Eisenmann, 1977; Zheng *et al.*, 1986; Bobev *et al.*, 2006).

The structure of the title compound can be viewed as a derivative of α-Mg$_3$Sb$_2$ (Loehberg, 1934; Martinez-Ripoll *et al.*, 1974), in which almost 70% of the Mg atoms occupying the tetrahedral position with Wyckoff position 2d (1/3, 2/3, z) are replaced by Zn atoms. This is supported not only by refinement of the structure with unconstrained occupancy on that site but also by the corresponding distances, which are much shorter than those observed in the related AMg$_2$Sb$_2$ compounds (A = Mg, Ca, Sr, Ba, Eu and Yb) (Deller & Eisenmann, 1977, Wartenberg *et al.*, 2002). Analogously, the refined distances are longer than those in AZn$_2$Sb$_2$ (Mewis, 1978), in good agreement with the Zn and Mg covalent radii (1.364 Å for Mg and 1.213 Å for Zn; Pauling, 1960). These experimental findings are well supported by the local bonding and site preference analyses (Zheng *et al.*, 1986; Burdett & Miller, 1990) based on band structure calculations.

Lastly, we point out that similar disorder of Mg and Zn has been proposed for the isostructural solid solution Mg$_{1.86}$Zn$_{1.14}$Sb$_2$ (Loehberg, 1934); however, this report erroneously suggests that Mg on both the octahedral and tetrahedral positions is replaced by Zn. Our refinement of Mg$_{1.59 (1)}$Zn$_{1.41 (1)}$Sb$_2$, which is the Zn-richer phase, unambiguously shows that the octahedral Mg position [Wyckoff symmetry 1a, (0,0,0) is not disordered.

Experimental

Handling of the pure metals and of the reaction mixtures was carried out either in an argon-filled glove-box or under vacuum. All starting materials were used as received: Mg (Alfa, turnings, 99.98% metal basis), Zn (Alfa, shot, 99.999%), Sb (Alfa, ingot, 99.99%). The synthesis was performed by loading the elements in a ratio Mg:Zn:Sb = 1:10:2 into an alumina crucible, which was subsequently sealed in an evacuated fused silica jacket. The reaction mixture was heated to 1273 K at a rate of 300 K h^{-1}, allowed to equilibrate at this temperature for 5 h, and cooled slowly to 873 K at a rate of 5 K h^{-1}. After reaching this temperature, it was removed from the furnace and

the excess of molten Zn was removed by centrifugation. Black, air-stable crystals of the title compound were the only product of this reaction.

Crystal data

Mg$_{1.59}$Zn$_{1.41}$Sb$_2$	D_x = 5.180 Mg m^{-3}
M_r = 374.32	Mo $K\alpha$ radiation
Trigonal, $P\bar{3}m1$	μ = 18.11 mm^{-1}
a = 4.3966 (9) Å	T = 120 (2) K
c = 7.171 (3) Å	Irregular fragment, black
V = 120.04 (6) Å^3	0.08 × 0.06 × 0.04 mm
Z = 1	

Data collection

Bruker SMART APEX diffractometer	1294 measured reflections
	118 independent reflections
ω scans	117 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	R_{int} = 0.023
T_{min} = 0.287, T_{max} = 0.482	θ_{max} = 26.1°

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.017P)^2]$
$R[F^2 > 2\sigma(F^2)]$ = 0.011	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2)$ = 0.029	$(\Delta/\sigma)_{max} < 0.001$
S = 1.29	$\Delta\rho_{max}$ = 0.37 e Å^{-3}
118 reflections	$\Delta\rho_{min}$ = −0.69 e Å^{-3}
10 parameters	

Table 1
Selected bond lengths (Å).

Mg—Sb	3.0403 (6)	Zn1/Mg1—Sb	2.7740 (13)
Zn1/Mg1—Sb^i	2.7470 (6)	Zn1/Mg1—Zn1/Mg1^{ii}	3.0685 (10)

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y + 1, -z + 1$.

In the structure refinement, the full occupancies for all sites were verified by freeing the site occupation factor for an individual atom, while the remaining occupation parameters were kept fixed. This proved that the Sb site (site symmetry 3m.) and one of the Mg sites (site symmetry $\bar{3}m$.) are fully occupied with deviations from full occupancy within 3σ. The second Mg site (site symmetry 3m.) refined with occupancy much higher than 100%. When Zn was refined in that position, the occupancy factor was significantly below unity. Therefore, this position (labeled Zn1/Mg1) was modeled as a statistical mixture of Zn and Mg, and refined as 70.3 (4)% Zn and 29.7 (4)% Mg.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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