Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

$Ta_{1.40(1)}Mn_{4.60(1)}Si_5$: distribution of the Ta and Mn atoms

Svilen Bobev,[a]* Eric D. Bauer[b] and John L. Sarrao[b]

[a]Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA, and [b]Materials Science and Technology Division, Los Alamos National Laboratory, MS K764, Los Alamos, NM 87545, USA

Correspondence e-mail: sbobev@chem.udel.edu

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(Si–Si) = 0.001 Å
Disorder in main residue
R factor = 0.019
wR factor = 0.048
Data-to-parameter ratio = 11.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 15 February 2006
Accepted 16 February 2006

The title compound is closely related to the previously described $Ta_2Mn_4Si_5$ structure which was studied by powder methods [Steinmetz & Roques (1977). *J. Less Common Metals*, **52**, 247–258]. The present single-crystal study shows a different ordering pattern of Ta and Mn over the metal sites and a small solid solubility range.

Comment

The binary silicides of transition metals have high thermal stability and many technologically important chemical and physical properties (Aronsson *et al.*, 1965, Samsonov & Vinitskii, 1980). Manganese silicides in particular have attracted considerable interest because of their application as high temperature thermoelectric materials and, more recently, studies of the cubic MnSi have shown fascinating magnetic and charge-transport properties (Manyala *et al.*, 2000).

Intrigued by the rich low-temperature physics of this chiral, cubic, MnSi compound, we attempted its synthesis using conventional laboratory equipment. However, because the corresponding binary Mn—Si phase diagram is rather complicated (Massalski, 1990), the synthesis of pure-phase material proved to be a difficult task. Even metal-flux techniques (Okada *et al.*, 2001) did not afford the formation of high-quality single crystals. In a subsequent attempt, stoichiometric amounts of high purity Si and Mn were enclosed in a Ta tube and reacted in an induction furnace. During the synthesis, incorporation of Ta occurred and the title compound was synthesized in high yield.

The ordered phase $Ta_2Mn_4Si_5$ with the body-centered orthorhombic V_6Si_5 (or Ti_6Ge_5) structure type (Pearson's

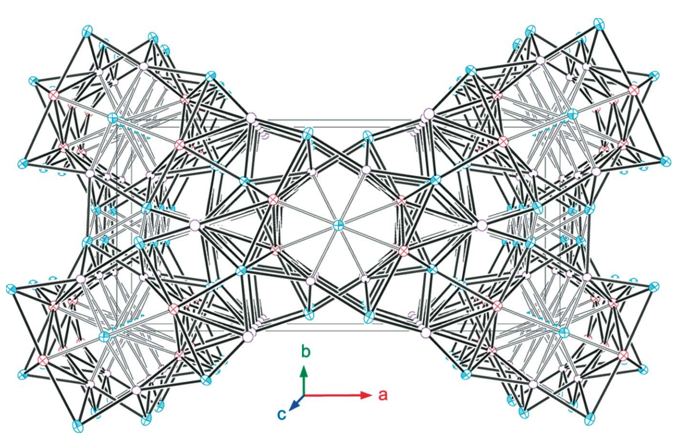

Figure 1
A view of the structure of (I), projected approximately along [001]. Displacement ellipsoids are drawn at the 95% probability level. Ta atoms are drawn as red ellipsoids with principal ellipses, Mn atoms as purple outline ellipsoids, and Si atoms as blue ellipsoids with octant shading. The bond-distance cut-off is 3 Å.

symbol *oI*44, Villars & Calvert, 1991) was recognized from powder X-ray diffraction nearly three decades ago (Steinmetz & Roques, 1977). The structure contains six crystallographically unique sites (three for Si and three for the transition metals), and can be viewed as densely packed layers of atoms (Fig. 1). The three sites available to the transition metals are of the same multiplicity (but different symmetry) and, if occupied by two different metals in an ordered manner, result in the formula $M_2M'_4Si_5$ as seen for $M_2Cr_4Si_5$ (M = Ti, Zr, Hf) (Crerar & Mar, 2004). The distribution of the metals over the three available sites in this phase has been studied by means of single-crystal X-ray diffraction and shown to be as in $Nb_2Cr_4Si_5$ (Kripyakevich *et al.*, 1968), *i.e.* Nb in one of the 8*j* (x, y, 0) sites, and Cr in the other 8*j* site and also in the 8*f* (x, 0, $\frac{1}{4}$) site (note that in some reports, the unit cell is given with the *a* and *b* axes interchanged, which changes the Wyckoff site label for the latter to 8*g*).

Steinmetz & Roques (1977), however, made a different assignment in their powder diffraction study of $Ta_2Mn_4Si_5$ and placed Ta in the 8*f* (or 8*g*) site and the two Mn atoms in the 8*j* sites. Analysis of the present structure shows that such distribution is not realistic since the atom in the 8*f* site would be at the center of a distorted octahedron of Si atoms with interatomic distances which are too short (2.3–2.5 Å) for normal Ta—Si contacts. However, these distances match nicely the sum of the Mn and Si atomic radii. Conversely, the site previously assigned to Mn2 (Wyckoff 8*j* with x, y, z = 0.142, 0.114, 0) is surrounded by seven Si atoms, but the distances are considerably longer (2.5–2.8 Å) and more appropriate for Ta—Si bonding. Based on these considerations, one might conclude that site assignments of Ta and Mn suggested by Steinmetz & Roques are incorrect, and the correct assignment has the two interchanged, as shown in Fig. 2. The structure refinements (Table 1) unequivocally confirm this conclusion, together with small solid solubility (Mn substituting at the Ta site), defining the formula of (I) as $Ta_{2-x}Mn_{4+x}Si_5$ (x = 0.6).

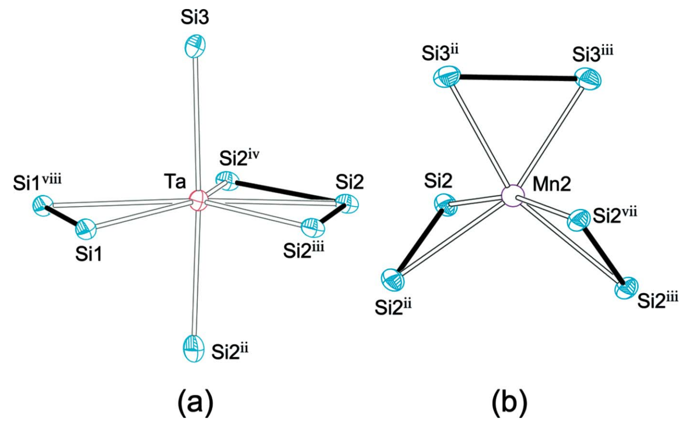

Figure 2
A view of the Si atom environments of (*a*) Ta, and (*b*) Mn2 in (I). Color code as in Fig. 1. Symmetry codes: (ii) $\frac{1}{2}-x, y-\frac{1}{2}, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (iv) $\frac{1}{2}-x, \frac{1}{2}-y, -\frac{1}{2}-z$; (vii) $x, -y, \frac{1}{2}+z$; (viii) $-x, -y, -z$.

Experimental

A mixture of Mn and Si (Alfa >99.99%) in the stoichiometry 1:1 was placed in a Ta tube and sealed by arc-welding. The sealed tube was heated in an induction furnace to 1373 K in increments of about 200 K over the course of 30 minutes. After the reaction temperature was achieved, the furnace was shut off and the reaction mixture was allowed to cool down. The recovered crystals of (I) were long needles (or better, thin rods) with dark-to-black metallic luster.

Crystal data

$Mn_{4.60}Si_5Ta_{1.40}$
M_r = 646.50
Orthorhombic, *Ibam*
a = 15.5206 (19) Å
b = 7.3856 (9) Å
c = 4.8852 (6) Å
V = 559.99 (12) Å^3
Z = 4
D_x = 7.668 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2157 reflections
θ = 2.6–28.7°
μ = 38.23 mm^{-1}
T = 100 (2) K
Needle, black
0.09 × 0.03 × 0.03 mm

Data collection

Bruker SMART APEX diffractometer
ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 2003)
T_{min} = 0.130, T_{max} = 0.319
2157 measured reflections
405 independent reflections
386 reflections with I > \2s(I)
R_{int} = 0.035
θ_{max} = 28.7°
h = −20 → 15
k = −9 → 9
l = −5 → 6

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.019
$wR(F^2)$ = 0.048
S = 1.12
405 reflections
34 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0257P)^2 + 0.8189P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 1.32 e Å^{-3}
$\Delta\rho_{min}$ = −1.15 e Å^{-3}

Table 1
Selected bond lengths (Å).

Mn1—Si3^{i}	2.327 (2)	Mn2—Si2^{iii}	2.4498 (15)
Mn1—Si2	2.3681 (19)	Mn2—Si2	2.4991 (15)
Mn1—Si3^{ii}	2.411 (2)	Ta—Si3	2.5205 (19)
Mn1—Si1^{iii}	2.4293 (8)	Ta—Si2	2.6149 (17)
Mn1—Si3^{iii}	2.7332 (9)	Ta—Si2^{ii}	2.6283 (18)
Mn2—Si3^{iii}	2.3889 (17)	Ta—Si1^{v}	2.6648 (4)
Mn2—Mn2^{iv}	2.4426 (3)	Ta—Si2^{iii}	2.7524 (8)

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{1}{2}, z$; (ii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z$; (iii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x, y, -z$; (v) $-x, -y, -z$.

The initial model was that of Steinmetz & Roques (1977). The cell orientation and naming of all atom sites was kept the same for the sake of easier comparison between the two structural models. The model with Ta at the 8*f* (x, 0, $\frac{1}{4}$) site yielded extremely poor residuals and abnormal displacement parameters for all the atoms. Next, the Ta and Mn 8*j* atoms were interchanged so that Ta was at (0.142, 0.117, 0) and Mn2 at (0.306, 0, $\frac{1}{4}$). This refinement readily converged with much improved residuals, but with unusual displacement parameters for Ta, suggestive of partial occupancy or Ta/Mn disorder on that site. This was confirmed by refining its site occupation, resulting in excellent residuals and a statistical distribution of Ta and Mn on this site in a ratio of 0.696 (4): 0.304 (4). The full occupancies for all the other sites were verified by freeing the site occupation factor for an individual atom, while other remaining parameters were kept fixed. The maximum difference peak and deepest difference hole are near Ta, distant by 0.80 Å and 1.42 Å, respectively.

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* (Sheldrick, 2001); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXL97*.

This work was funded by a University of Delaware start-up grant. Work at LANL is done under the auspicies of US DOE.

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