opposite O atoms are O(2)–O(3) = 3·180 (3) and O(1)–O(2) = 3·065 (3) Å; the Ca^{2+} ions are located in cages situated between two successive windows where they realize a 6 + 2 coordination with O atoms and Ca–O distances similar to those observed in α-$Ca_2P_2O_7$ (Table 2). Systematic geometrical calculations prove there is no pathway for the Ca^{2+} (or Mg^{2+}) ions through the framework. The coordination about Cu and Ca is geometrically quite different but the substitution of one Cu^{2+} for one Ca^{2+} is possible, involving a decrease of the lattice volume: 574·77 and 518·10 $Å^3$ for α-$Ca_2P_2O_7$ and $CaCuP_2O_7$, respectively. However, a progressive substitution of Cu^{2+} for Ca^{2+} is not expected due to the different behaviour of the two metals especially in their coordination with oxygen. In MoP_2O_7 (Leclaire, Borel, Grandin & Raveau, 1988) the arrangement of the $[MoO_6]$ octahedra and the $[P_2O_7]$ groups is similar to that of the $[CuO_5]$ pyramids and the diphosphate groups in $CaCuP_2O_7$, but the layers are staggered and so the tunnels are not linear contrary to those of $CaCuP_2O_7$.

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Structure of Ta_5SnGa_2

By Jinhua Ye and Hiroyuki Horiuchi

Mineralogical Institute, University of Tokyo, Hongo 7-3-1, *Tokyo* 113, *Japan*

and Toetsu Shishido, Kazutoshi Ukei and Tsuguo Fukuda

Institute for Materials Research, Tohoku University, Katahira, Sendai 980, *Japan*

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Abstract. Digallium pentatantalum tin, M_r = 1162·87, tetragonal, *I*4/*mcm*, a = 10·354 (2), c = 5·1795 (6) Å, V = 555·3 $Å^3$, Z = 4, D_x = 13·91 Mg m^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 118·2 mm^{-1}, $F(000)$ = 1908, room temperature, final R = 0·053, wR = 0·055 for 336 $[|F_o| > 3\sigma(F_o)]$ unique reflections. The title compound is isomorphous with W_5Si_3. The main characteristic of the structure is the existence of $(Ga_2Ta_8)_\infty$ columns parallel to the c axis. These columns are connected by Sn and Ga atoms to form a three-dimensional framework. There are two distinct sites for Ga atoms with one of them being shared equally and statistically between Ga and Sn atoms.

Introduction. In the project to study the crystal chemistry, structure and superconductivity of V*a*–Sn–Ga (V*a* = Ta, Nb, V) ternary systems, we have recently succeeded in synthesizing single crystals of a new ternary compound, Ta_5SnGa_2, in the Ta–Sn–Ga system (Shishido, Ye, Toyota, Ukei, Sasaki, Horiuchi & Fukuda, 1989). The present paper reports the crystal structure of this compound. Studies on the other members of the systems have also been made; the crystal growth and structure have been reported for Nb–Sn–Ga by Ukei, Shishido & Fukuda (1989) and for V–Sn–Ga by Ye, Horiuchi, Shishido & Fukuda (1990).

Experimental. Ta_5SnGa_2 crystals were synthesized by the self-component flux method from the melt of Ta, Sn and Ga (Shishido *et al.*, 1989). The crystal used for the single-crystal X-ray work was a cube with side ~0·04 mm. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The lattice parameters were determined from 25 reflections with $28 < 2\theta < 36°$. A total of 2554 reflections in the range $2 < 2\theta < 70°$ ($-16 \le h \le 16$, $-16 \le k \le 16$, $0 \le l \le 8$) were collected under the following conditions: ω–2θ scan, scan width $\Delta\omega = (1·1 + 0·4\tan\theta)°$, scan speed 0·5° min^{-1}. The intensities of

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Table 1. *Atomic parameters for* Ta_5SnGa_2

$B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	Wyckoff notation	Occupancy	x	y	z	B_{eq}(Å^2)
Ta(1)	16(*k*)	1·0	0·0734 (1)	0·2208 (1)	0	0·64
Ta(2)	4(*b*)	1·0	0	$\frac{1}{2}$	$\frac{1}{4}$	0·68
Ga	4(*a*)	1·0	0	0	$\frac{1}{4}$	0·58
MX	8(*h*)	0·5Sn, 0·5Ga	0·3322 (4)	0·1678 (4)	0	0·65

Table 2. *Interatomic distances* (Å) *and angles* (°)

Ta(1)—Ta(1^{i})	3·0027 (9)	Ta(1)—Ta(1^{ii})	3·013 (2)
Ta(1)—Ta(1^{iii})	3·372 (1)	Ta(1)—Ta(1^{iv})	3·407 (2)
Ta(1)—Ta(2)	3·257 (1)	Ta(1)—Ga	2·735 (1)
Ta(1)—*MX*	2·735 (5)	Ta(1)—*MX*^{iii}	2·999 (3)
Ta(1)—*MX*^{iv}	2·751 (5)	Ta(2)—Ta(2^{v})	2·5898 (3)
Ta(2)—*MX*^{iv}	2·777 (4)	Ga—Ga^{v}	2·5898 (3)
Ga—*MX*	4·065 (5)	*MX*-*MX*^{iii}	3·536 (5)
Ta(1^{i})—Ta(1)—Ta(1^{iii})	64·32 (3)	Ta(1^{iv})—Ta(1)—Ta(1^{vi})	90
Ta(1)—Ta(2)—Ta(1^{i})	54·89 (3)	Ta(1)—Ta(2)—Ta(1^{ii})	55·10 (3)
MX^{iii}—Ta(2)—*MX*^{iv}	102·6 (1)	Ta(1)—Ga—Ta(1^{i})	66·58 (3)
Ta(1)—Ga—Ta(1^{iii})	76·09 (3)	Ta(1)—Ga—Ta(1^{iv})	77·05 (3)

Symmetry code: none x,y,z; (i) $1-x,y,\frac{1}{2}-z$; (ii) $\frac{1}{2}-y,\frac{1}{2}-x,1-z$; (iii) $y,x,\frac{1}{2}-z$; (iv) $1-y,\ x,z$; (v) $-x,-y,-z$; (vi) $y,1-x,z$.

004 and 550 were monitored after every 100 measurements and showed no significant fluctuations. 336 unique reflections with $|F_o| > 3\sigma$ were obtained after averaging equivalent ones. Lorentz–polarization and absorption corrections were carried out. Transmission factors were in the range 0·063 to 0·104.

Structure analyses were performed with the least-squares program *RFINE*2 (Finger, 1969). The atomic coordinates of W_5Si_3 (Aronsson, 1955) were used as initial parameters. Scattering factors of neutral atoms with correction for anomalous dispersion were from *International Tables for X-ray Crystallography* (1974). Refinement in space group *I*4/*mcm*, minimizing $\sum w(\Delta F)^2$ with $w = 1/\sigma^2(F)$, gave final agreement indices $R = 0{\cdot}053$, $wR = 0{\cdot}055$. $(\Delta/\sigma)_{max} = 0{\cdot}23$. The final difference electron density map had maxima and minima of $\pm 8{\cdot}0\ e\ Å^{-3}$. The secondary-extinction coefficient was refined to $g_{iso} = 0{\cdot}57 \times 10^{-9}$.

Discussion. Final atomic parameters are given in Table 1 with selected interatomic distances and angles in Table 2.* A projection of the atomic arrangement along the *c* axis is shown in Fig. 1.

There are four kinds of atom sites in the structure. The 16(*k*) and 4(*b*) sites are both occupied by Ta atoms, the 4(*a*) site by Ga atoms and the 8(*h*) site by Ga and Sn atoms. The Ga atom in the 4(*a*) site is coordinated by eight Ta atoms, which form the apices of a truncated Archimedean antiprism. Such antiprisms share common faces formed by four Ta atoms to make a $(Ga_2Ta_8)_\infty$ column, which is centered on the fourfold axis. These columns are linked together by Sn and Ga atoms which are illustrated with shaded circles in Fig. 1.

The three-component diagram of Ta–Sn–Ga is as yet unknown and Ta_5SnGa_2 is the first ternary compound found in this system. The structure of this compound is very similar to that of the binary compound Ta_5Ga_3, which also crystallizes in the W_5Si_3-type structure (Meissner & Schubert, 1965). However, no compound like Ta_5Sn_3 has ever been reported. In the study on the crystal growth of the title ternary compound (Shishido *et al.*, 1989), it has been shown that the chemical formula of the grown crystals is very close to Ta_5SnGa_2 even if the starting materials were prepared with Ta:Ga in the atomic ratio of 3:1 and 3:2. This fact means that the solid-solution range of the Ta_5SnGa_2 compound is quite narrow. However, further investigations will be needed to make clear whether the successive substitution of Ga by Sn atoms between Ta_5Ga_3 and Ta_5SnGa_2 compounds is possible.

Compared with the binary compound Ta_5Ga_3, some of the Ga atoms in the title compound are substituted by Sn atoms. The structure analysis has made it clear that Sn atoms only substitute the Ga atoms in 8(*h*) sites, not those at 4(*a*) sites. It is worth noting that only half of the Ga atoms in 8(*h*) sites are

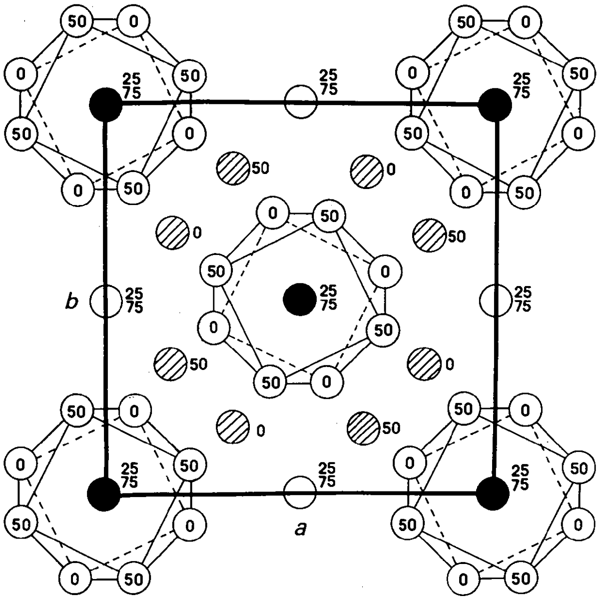

Fig. 1. Projection of the crystal structure of Ta_5SnGa_2 along the *c* axis. Atom key: open circles Ta, filled circles Ga, shaded circles *MX*. Numbers correspond to *z* parameters.

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* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52686 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

substituted by Sn atoms, while in another V*a*–Sn–Ga (V*a* = Ta, Nb, V) system compound, Nb_5Sn_2Ga, the 8(*h*) sites are all substituted by Sn atoms (Ukei *et al.*, 1989). The common point of the structures of these two compounds is that the 4(*a*) sites, at the centers of the Archimedean antiprisms, are always occupied by Ga atoms. This fact indicates that Ga atoms have a strong tendency to be coordinated by V*a* atoms to form a kind of polyhedron which characterizes the structure.

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Structure of V_2Sn_2Ga

By Jinhua Ye and Hiroyuki Horiuchi

Mineralogical Institute, University of Tokyo, Hongo, Tokyo 113, *Japan*

and Toetsu Shishido and Tsuguo Fukuda

Institute for Materials Research, Tohoku University, Katahira, Sendai 980, *Japan*

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Abstract. Gallium ditin divanadium, $M_r = 408{\cdot}98$, orthorhombic, *Acam*, $a = 6{\cdot}7191\ (7)$, $b = 18{\cdot}798\ (2)$, $c = 5{\cdot}603\ (1)$ Å, $V = 707{\cdot}7$ Å^3, $Z = 8$, $D_x = 7{\cdot}68$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 27{\cdot}0$ mm^{-1}, $F(000) = 1416$, room temperature, final $R = 0{\cdot}044$, $wR = 0{\cdot}054$ for 794 unique reflections with $|F_o| > 3\sigma(F_o)$. The crystal structure of the title compound is a new type. It consists of two kinds of bands of linked GaV_5 pentagons and Sn-atom clusters which alternate along the *b* axis.

Introduction. V–Sn–Ga is a member of V*a*–Sn–Ga (V*a* = Ta, Nb, V) ternary systems, which have been the subject of our interest because most of the binary compounds composed of V*a*, Sn and Ga elements exhibit superconductivity, and also because the three-component diagrams of V*a*–Sn–Ga systems are not known. Research on the Ta–Sn–Ga system has been carried out by Ye, Horiuchi, Shishido, Ukei & Fukuda (1990) and on another member, Nb–Sn–Ga, by Ukei, Shishido & Fukuda (1989). In this work, we focused our concern on the V–Sn–Ga system and succeeded in synthesizing single crystals of V_2Sn_2Ga for the first time in the same way as that applied in the compounds of the Ta–Sn–Ga and Nb–Sn–Ga systems. Details of crystal growth and physical properties will be presented elsewhere. Here, we describe the structure determination of the title compound.

Experimental. Single crystals were synthesized by the self-component flux method (Shishido, Ye, Toyota, Ukei, Sasaki, Horiuchi & Fukuda, 1989). The crystal used for the single-crystal X-ray diffraction study was about $0{\cdot}12 \times 0{\cdot}06 \times 0{\cdot}21$ mm in size. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The lattice parameters were refined from 25 reflections with $25 < 2\theta < 35°$. A total of 3212 reflections in the range $2 < 2\theta < 70°$ ($-10 \leq h \leq 10$, $-30 \leq k \leq 30$, $0 \leq l \leq 9$) were collected under the following conditions: ω–2θ-scan mode, scan width $\Delta\omega = (1{\cdot}1 + 0{\cdot}4\tan\theta)°$, scan speed ($2\theta$) 4° min^{-1}. Two standard reflections, measured at an interval of 100 reflections, showed no significant fluctuation in intensity. Reflection data were corrected for Lorentz–polarization effects and an empirical absorption correction was applied. The minimum and maximum transmission factors were 0·26 and 0·51, respectively. After the above corrections, the intensities of symmetrically equivalent reflections were averaged to give 794 unique reflections with $|F_o| > 3\sigma(F_o)$.

The structure was solved with the aid of Patterson and Fourier syntheses. Full-matrix least-squares refinement of variable atomic coordinates with anisotropic temperature factors and an isotropic extinction coefficient, minimizing $\sum w(\Delta F)^2$ with $w = 1/\sigma^2(F_o)$, converged to $R = 0{\cdot}044$, $wR = 0{\cdot}054$ for

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