

The Li atom is tetrahedrally coordinated by one water molecule O(*W1*) and three external O atoms O(*E11*), O(*E21*) and O(*E12*) belonging to two $\text{P}_6\text{O}_{18}^{6-}$ ring anions. The LiO_4 tetrahedron is as regular as the PO_4 tetrahedron. Within a sphere coordination of 3.5 Å, the two ammonium cations have different environments, namely N(1) O_5 and N(2) O_6 . The first, N(1), is coordinated to one water molecule O(*W2*) and four external O atoms [O(*E21*), O(*E22*), O(*E31*), O(*E32*)] belonging to three P_6O_{18} rings. O(*E21*) is a vertex common to an LiO_4 tetrahedron and an N(1) O_5 polyhedron. The second, N(2), has sixfold coordination, formed by two water molecules [O(*W1*), O(*W2*)] and four O atoms [O(*E11*), O(*L12*), O(*E31*), O(*E22*)] from two P_6O_{18} rings. The N(2) O_6 distorted octahedron and LiO_4 tetrahedron contact one another *via* the common edge O(*E11*)—O(*W1*). The N(1) O_5 and N(2) O_6 polyhedra are interconnected by the LiO_4 tetrahedra (Fig. 2). The alternating N(1) O_5 , LiO_4 and N(2) O_6 form chains running along the *b* axis. The shortest N(2)—Li, Li—N(1) and N(1)—N(2) distances and the largest N(1)—N(2)—Li, N(2)—Li—N(1) and Li—N(1)—N(2) angles are,

respectively, 3.590 (6), 3.994 (6) and 4.438 (4) Å for the bonds and 133.3 (1), 169.4 (2) and 165.3 (1)° for the angles. So the P_6O_{18} ring anions are interconnected by the LiO_4 tetrahedron, the two ammonium polyhedra and the hydrogen bonds, forming the $\text{Li}_2(\text{NH}_4)_4\text{P}_6\text{O}_{18}\cdot 4\text{H}_2\text{O}$ three-dimensional network.

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Structure of $\text{Nb}_5(\text{Ge}_x\text{Sn}_{1-x})_2\text{Ge}$, $x = 0.25$

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Abstract. $\text{Nb}_5\text{Ge}_{1.5}\text{Sn}_{1.5}$, $M_r = 751.45$, tetragonal, $I4/mcm$, $a = 10.451$ (1), $c = 5.1920$ (7) Å, $V = 567.0$ (1) Å³, $Z = 4$, $D_x = 8.80$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 24.05$ mm⁻¹, $F(000) = 1312$, room temperature, final $R = 0.044$, $wR = 0.042$ for 245 [$|F_o| > 3\sigma(F_o)$] unique reflections. The title compound is isomorphous with W_5Si_3 . The 16(*k*) and 4(*a*) sites are only occupied by Nb, and the 4(*b*) sites only by Ge. The 8(*h*) sites are randomly occupied by atoms of both Ge and Sn with an atomic ratio of 1:3. Atoms with large atomic radii are not accommodated by the 4(*a*) sites in a W_5Si_3 -type structure.

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Introduction. The intermetallic compounds in the Nb–Sn–Ge ternary system are studied because of the possibility of their being superconductive materials. But as yet, not many compounds in this system have been synthesized. So the synthesis of the compounds in the system was performed and single crystals of a new compound of composition Nb:Sn:Ge = 10:3:3 were obtained. The crystal structure was analyzed by a single-crystal X-ray diffraction method. This paper reports the results of the crystal-structure analysis.

Experimental. Crystals of $\text{Nb}_5(\text{Ge}_x\text{Sn}_{1-x})_2\text{Ge}$, $x = 0.25$, were synthesized by the self-component flux method (Sn as flux). Nb and Ge were mixed with an atomic ratio of 3:1 and Sn was added to these

mixtures with a weight ratio of 5:1. The mixture was placed in an alumina crucible and heated in an He flow. The mixture was heated to 1673 K at a rate of 400 K h⁻¹ and was held for 10 h at this temperature. It was slowly cooled to 1273 K at 1 K h⁻¹ and then rapidly cooled to room temperature. The crystals were separated by dissolving Sn in dilute hydrochloric acid.

The crystals were observed with a scanning electron microscope (SEM) and the chemical composition was analyzed using an energy-dispersive X-ray analyser (EDX). The chemical composition was determined to be Nb₅(Ge_x,Sn_{1-x})₂Ge; $x = 0.25$ (Ge:Sn = 1:1).

The crystal used for structure analysis was a cube with edges of 0.05 mm. An X-ray photograph showed diffraction symmetry 4/*mmm* with systematic absences $h + k + l = 2n + 1$ and $l = 2n + 1$ for $h0l$ and $0kl$, and the structure was considered to be analogous to Nb₅SnGa₂ (Ye, Horiuchi, Shishido, Ukei & Fukuda, 1990) with a W₅Si₃-type structure (Aronsson, 1955). Possible space groups are $\bar{I}4c2$, $I4cm$ and $I4/mcm$. Intensity data were collected on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The lattice parameters were determined by 20 reflections of $15 < 2\theta < 36^\circ$. 1746 reflections ($-15 < h < 15$, $0 < k < 15$, $-8 < l < 8$, $5 < 2\theta < 60^\circ$) were obtained under the following conditions: ω - 2θ scan, scan width $\Delta\omega = (1.70 + 0.65\tan\theta)^\circ$ and scan speed 2° min^{-1} . Two standard reflections, 660 and 004, were measured every 100 reflections and their intensities showed no considerable fluctuations throughout the measurement. Max. $(\sin\theta)/\lambda = 1.2186 \text{ \AA}^{-1}$. The intensities of equivalent reflections confirmed the above possible space groups. Lorentz-polarization corrections were carried out during data collection. Corrections for absorption and extinction were not performed as their effects were negligible. 245 unique reflections with $|F_o| > 3\sigma(F_o)$ were finally obtained by averaging equivalent reflections and were used for crystal-structure analysis.

The least-squares program *RFINE2* (Finger, 1969) was used for crystal structure refinements. The atomic coordinates of Nb₅SnGa₂ (Ye *et al.*, 1990) were used as initial parameters. Refinement minimizing $\sum w(\Delta F)^2$, with $w = 1/\sigma^2(F)$, was carried out. The atomic positions, anisotropic temperature factors and occupancy values of Ge and Sn atoms for 4(*b*) and 8(*h*) sites were refined. $I4/mcm$ was finally confirmed by the results of structure analysis.

The final agreement indices were $R = 0.044$, $wR = 0.042$. $(\Delta/\sigma)_{\text{max}} = 0.000125$. In the final difference Fourier synthesis, maximum and minimum heights were 6.0 and $-6.0 e \text{ \AA}^{-3}$, respectively. Atomic scattering factors with anomalous dispersion of

Table 1. Atomic parameters for Nb₅(Ge_x,Sn_{1-x})₂Ge, $x = 0.25$

$$B_{\text{eq}} = (4/3)\sum_i\sum_j\beta_{ij}a_i \cdot a_j$$

Wyckoff notation	Occupancy	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
Nb(1) 16(<i>k</i>)	1.0	0.0733 (1)	0.2204 (1)	0	0.40
Nb(2) 4(<i>a</i>)	1.0	0	0.5	0.25	0.42
Ge 4(<i>b</i>)	1.0	0	0	0.25	0.31
(Sn,Ge) 8(<i>h</i>)	0.75Sn,0.25Ge	0.1674 (1)	0.6674 (1)	0	0.50

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

Nb(1)—Nb(1 ⁱ)	3.015 (1)	Nb(1)—Nb(1 ⁱⁱ)	3.049 (2)
Nb(1)—Nb(1 ⁱⁱⁱ)	3.386 (1)	Nb(1)—Nb(1 ^{iv})	3.433 (2)
Nb(1)—Nb(2)	3.288 (1)	Nb(1)—Ge	2.753 (1)
Nb(1)—SnGe ^v	2.766 (1)	Nb(1)—SnGe ^{vi}	3.0134 (7)
Nb(1)—SnGe ^{vii}	2.775 (1)	Nb(2)—Nb(2 ^{viii})	2.5960 (3)
Nb(2)—SnGe ^{viii}	2.7935 (7)	Ge—Ge ^v	2.5960 (3)
Ge—SnGe ^{ix}	4.1021 (6)	SnGe ^v —SnGe ^{vii}	3.564 (1)
Nb(1 ^{iv})—Nb(1)—Nb(1 ⁱⁱⁱ)	64.56 (2)	SnGe ^{vii} —Nb(2)—SnGe ^{viii}	102.46 (1)
Nb(1 ^{iv})—Nb(1)—Nb(1 ^v)	90.0	Nb(1)—Ge—Nb(1 ⁱ)	66.40 (3)
Nb(1)—Nb(1)—Nb(1 ⁱ)	54.57 (2)	Nb(1)—Ge—Nb(1 ⁱⁱⁱ)	75.90 (4)
Nb(1)—Nb(1)—Nb(1 ⁱⁱ)	55.24 (4)	Nb(1)—Ge—Nb(1 ^{iv})	77.15 (1)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - y, \frac{1}{2} - x, -z$; (iii) $y, x, \frac{1}{2} - z$; (iv) $-y, x, z$; (v) $-x, -y, -z$; (vi) $y, -x, z$; (vii) $x, -y, \frac{1}{2} - z$; (viii) $-x, -y, z$.

neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are given in Table 1,* and selected interatomic distances and angles are shown in Table 2. Fig. 1 shows the crystal structure projected along the c and a axes. The crystal structure of Nb₅(Ge_x,Sn_{1-x})₂Ge, $x = 0.25$, is isomorphous with W₅Si₃ (Aronsson, 1955). This structure has four kinds of atomic site: 16(*k*), 8(*h*), 4(*a*) and 4(*b*). Both 16(*k*) and 4(*b*) sites are occupied by Nb, the 4(*a*) site by Ge only and the 8(*h*) site by both Ge and Sn in a disordered manner with a ratio of 1:3. Ge atoms are located at both the 4(*a*) and the 8(*h*) sites but Sn is accommodated by the 8(*h*) site only. Thus, the chemical formula is considered to be Nb₅(Ge_x,Sn_{1-x})₂Ge with $x = 0.25$, compared with the chemical formula of Ta₅SnGa₂ (Ye *et al.*, 1990) which has been structurally shown to be Ta₅(Ga_x,Sn_{1-x})₂Ga with $x = 0.5$. In the title compound, Ge in the 4(*a*) site is coordinated by eight Nb atoms, the Nb atoms forming a decahedron. The decahedra share their faces with each other and make columns along the c axis. Fourfold axes run through the centers of the columns. These columns are connected to each other by Nb at 4(*b*) and (Sn,Ge).

* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55646 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

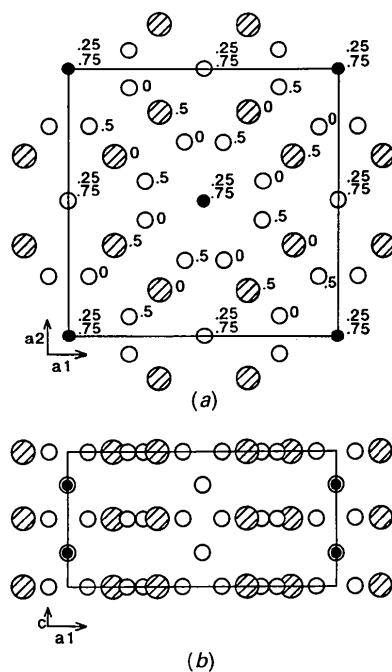


Fig. 1. The crystal structure of $\text{Nb}_5(\text{Ge}_x\text{Sn}_{1-x})_2\text{Ge}$, $x = 0.25$, projected (a) along the c axis and (b) along the a axis; open circles Nb, filled circles Ge, shaded circles (Sn, Ge).

It is considered that the arrangement of Ge and Sn atoms in the structure is controlled by their atomic radii. The analysis shows that Sn was not accommodated in the $4(a)$ site, but this site is occupied by Ge. The atomic radii of the Sn atoms are relatively large compared with the small radius of Ge atoms. Thus, the $4(a)$ site with its restricted space is expected to be occupied by the smaller atoms. Sn atoms of other W_5Si_3 -type intermetallic compounds, Ta_5SnGa_2 (Ye *et al.*, 1990), $\text{Nb}_5\text{Sn}_2\text{Ga}$ (Ukei, Shishido & Fukuda, 1989) and $\text{Nb}_5\text{Sn}_2\text{Si}$ (Horyn &

Lukaszewicz, 1970), show the same crystal chemical behavior as Sn in the present structure. That, in these compounds, Sn atoms are always accommodated in $8(h)$ sites. In binary systems of Va–Sn, such as Nb–Sn, Ta–Sn or V–Sn, compounds which have crystallized in a W_5Si_3 -type structure have not been reported. This may be because W_5Si_3 -type structures are unstable when containing large atoms.

The title compound has an interesting chemical composition, with $\text{Ge}/\text{Sn} = 1$. If Sn atoms occupy all the $8(h)$ sites, the chemical formula should be $\text{Nb}_5\text{Sn}_2\text{Ge}$ for $\text{Nb}_5(\text{Ge}_x\text{Sn}_{1-x})_2\text{Ge}$ with $x = 0$. However, the title compound never contains this amount of Sn atoms for the synthetic condition of the Sn self-flux method. This compound contains as many Sn atoms as the crystal structure allows. As a conclusion, the amount of Sn in the chemical composition seems to be governed by the space around the Nb atoms.

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Single-Crystal Structure of $\text{K}_3\text{Nb}_8\text{O}_{21}$

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Abstract. Tripotassium 21-oxooctaniobate, $M_r = 1196.53$, hexagonal, $P6_3/mcm$, $a = 9.1584$ (5), $c = 12.0404$ (4) Å, $V = 874.6$ (1) Å³, $Z = 2$, $D_x = 4.54$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 5.65$ mm⁻¹, $F(000) = 1106$, $T = 294$ K, $R = 0.044$, $wR = 0.047$ for 2540 reflections with $I > 3\sigma(I)$. The

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