

Experimental

The crystal was prepared from material obtained from Auerbach, Oberpfalz, Bavaria, Germany.

Crystal data

Y _{0.947} Dy _{0.028} Er _{0.018} Gd _{0.007} - PO ₄ ·2H ₂ O	Synchrotron radiation
M _r = 223.85	λ = 0.9998 Å
Monoclinic	Cell parameters from 33 reflections
l ₂ /a	θ = 9.5–24°
a = 5.578 (1) Å	μ = 15.48 mm ⁻¹
b = 15.006 (3) Å	T = 293 K
c = 6.275 (2) Å	Needle
β = 117.83 (2)°	0.1130 × 0.0054 ×
V = 464.5 (2) Å ³	0.0040 mm
Z = 4	Colourless
D _x = 3.20 Mg m ⁻³	

Data collection

Stoe five-circle (HASYLAB) diffractometer	R _{int} = 0.083
Profile data from ω scans (0.02° steps, 95 steps/reflection, 1.5 s/step)	θ _{max} = 49.9°
Absorption correction: analytical	h = -7 → 8
T _{min} = 0.45, T _{max} = 0.93	k = 0 → 21
1335 measured reflections	l = -9 → 8
743 independent reflections	1 standard reflection
637 observed reflections	frequency: 45 min
[F > 3.0σ(F)]	intensity variation: 3.3%

Refinement

Refinement on F	Δρ _{max} = 1.8 e Å ⁻³
R = 0.077	Δρ _{min} = -2.4 e Å ⁻³
wR = 0.052	Extinction correction: Type 1
S = 1.742	Gaussian isotropic (Becker & Coppens, 1974)
644 reflections	Extinction coefficient: 15080
39 parameters	Atomic scattering factors
H-atom parameters not refined	from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.4.6B)
w = 1/σ ² (F)	
(Δ/σ) _{max} < 0.001	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
Y	1/4	0.8289 (1)	0	0.0059 (5)
P	1/4	0.3307 (3)	0	0.013 (1)
O1	0.302 (1)	0.3857 (5)	0.224 (1)	0.020 (3)
O2	0.506 (1)	0.2714 (5)	0.084 (1)	0.015 (3)
O3	0.630 (2)	0.0680 (5)	0.218 (1)	0.022 (4)

Table 2. Selected geometric parameters (Å, °)

Y—O1 ⁱ	2.434 (6)	O1—O2 ⁱⁱⁱ	2.56 (1)
Y—O2 ⁱⁱ	2.251 (6)	O1—O1 ⁱⁱⁱ	2.59 (1)
Y—O2 ⁱ	2.470 (7)	O1—O3 ^v	2.690 (7)
Y—O3 ⁱⁱ	2.360 (7)	O1—O3 ⁱ	2.76 (1)
P—O1	1.536 (8)	O2—O2 ⁱⁱⁱ	2.547 (7)

P—O2	1.550 (6)	O2—O2 ^v	2.622 (7)
O1—O2	2.44 (1)	O2—O1 ⁱⁱⁱ	2.56 (1)
O1—P—O1 ⁱⁱⁱ	115.0 (5)	O1—P—O2	104.3 (4)
O2—P—O2 ⁱⁱⁱ	110.0 (4)	O1—P—O2 ⁱⁱⁱ	111.7 (3)

Symmetry codes: (i) 1 - x, ½ + y, ½ - z; (ii) 1 - x, 1 - y, 1 - z; (iii) ½ - x, y, -z; (iv) ½ - x, ½ - y, ½ - z; (v) ¾ - x, ½ - y, ½ - z.

Data collection and cell refinement: *DIF4* (Stoe & Cie, 1985). Data reduction: local program; *SHELX76* (Sheldrick, 1976). Program(s) used to solve structure: *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). Program(s) used to refine structure: *PROMETHEUS*.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: NA1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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NaVS₂O₆

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Abstract

The structure of sodium vanadium metasilicate, NaVS₂O₆, has been determined from diffractometer data. The structure is similar to that of jadeite (NaAlSi₂O₆). Comparison of a new crystal structure refinement for NaVS₂O₆ with published refinements for ten NaM³⁺Si₂O₆ pyroxenes indicates that the O1—Si—

O2 angles correlate with the differences $d_{br-nbr} = \text{mean } \langle \text{Si—O}(br) \rangle - \text{mean } \langle \text{Si—O}(nbr) \rangle$ ($br = \text{bridging}$, $nbr = \text{nonbridging}$) in such a way as to follow two different trends. One is for the Sc–Ti–V–Cr series and the other for the Fe–Mn–Ga series of compounds.

Comment

The title compound is isostructural with $\text{NaAlSi}_2\text{O}_6$, $\text{NaCrSi}_2\text{O}_6$ and $\text{NaFeSi}_2\text{O}_6$ (Clark, Appleman & Papike, 1969), $\text{NaScSi}_2\text{O}_6$ (Hawthorne & Grundy, 1973), $\text{NaInSi}_2\text{O}_6$ (Hawthorne & Grundy, 1974), $\text{NaTiSi}_2\text{O}_6$ (Ohashi, Fujita & Osawa, 1982), $\text{NaGaSi}_2\text{O}_6$ (Ohashi,

Fujita & Osawa, 1983) and $\text{NaMnSi}_2\text{O}_6$ (Ohashi, Osawa & Tsukimura, 1987).

The dependence of the Si—O distances on the size and electronegativity of the octahedral M^{3+} ion was examined for the $\text{Na}M^{3+}\text{Si}_2\text{O}_6$ pyroxenes by Ohashi, Osawa & Sato (1990). Generally, the mean Si—O distance increases with an increase in the radius of the M^{3+} ion. In the Sc–Ti–V–Cr–Al series, the size of the M^{3+} ion affects Si—O(bridging) and Si—O(nonbridging) equally. On the other hand, in the In–Fe–Mn–Ga series, the size of the M^{3+} ion affects only Si—O(bridging). d_{br-nbr} decreases with increasing electronegativity of the M^{3+} ion in the Sc–Ti–V–Cr–Al series, where $d_{br-nbr} = \text{mean } \langle \text{Si—O}(br) \rangle - \text{mean } \langle \text{Si—O}(nbr) \rangle$, $\text{mean } \langle \text{Si—O}(br) \rangle = 1/2(\text{Si—O}3A1 + \text{Si—O}3A2)$ and $\text{mean } \langle \text{Si—O}(nbr) \rangle = 1/2(\text{Si—O}1 + \text{Si—O}2)$.

The O1—Si—O2 angle is the largest O—Si—O angle in each compound. The largest O1—Si—O2 angles may be due in part to the greater repulsion between the more negatively charged nonbridging O atoms. Table 3 summarizes the differences, d_{br-nbr} , and the O1—Si—O2 angles in $\text{Na}M^{3+}\text{Si}_2\text{O}_6$ pyroxenes. As shown in Fig. 3, with the exception of the smallest Al and the largest In compounds, the O1—Si—O2 angle correlates with d_{br-nbr} in such a way that they follow two different trends: that of the Sc–Ti–V–Cr series and that of the Fe–Mn–Ga series. In the former, the octahedral ($M1$) sites are occupied by lower electron-density ions, whereas in the latter the octahedral ($M1$) sites are occupied by higher electron-density ions.

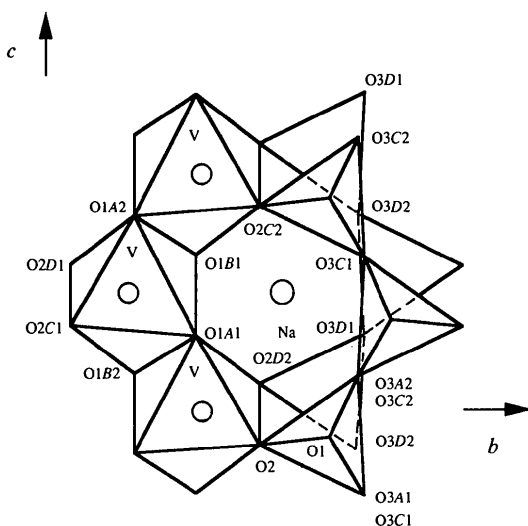


Fig. 1. a^* -axis projection of NaVSi_2O_6 . Atom labelling follows that used by Clark, Appleman & Papike (1969).

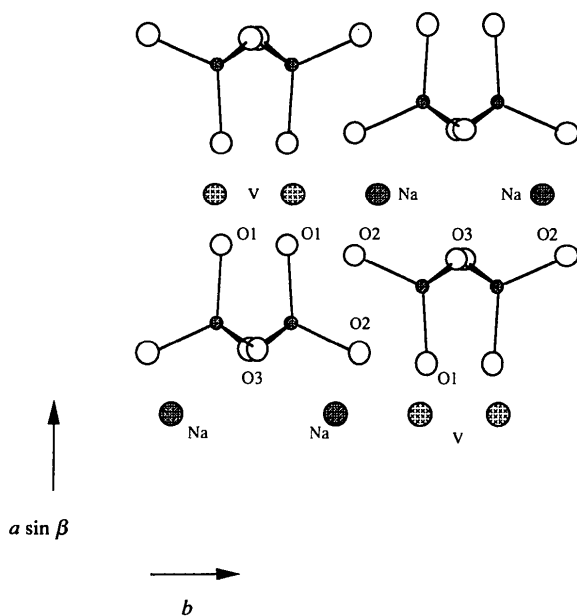


Fig. 2. c -axis projection of NaVSi_2O_6 .

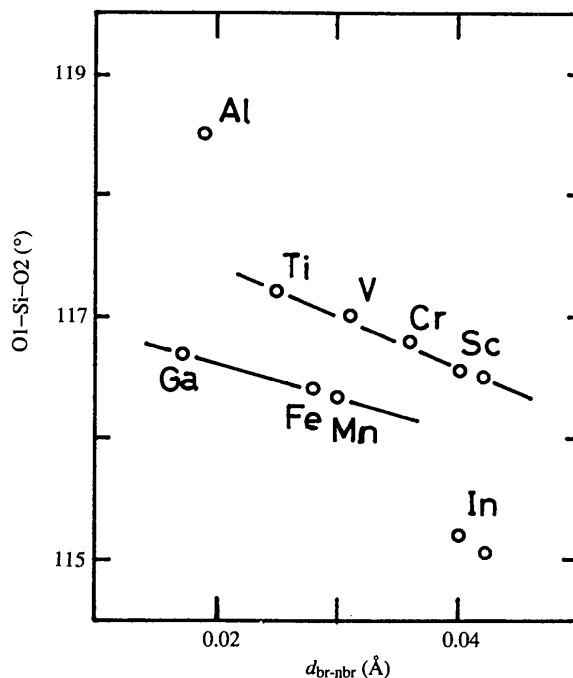


Fig. 3. The variation of the O1—Si—O2 angle ($^\circ$) with d_{br-nbr} (Å) for the $\text{Na}M^{3+}\text{Si}_2\text{O}_6$ pyroxenes.

Experimental

The title compound was prepared by solid-state reaction using a belt-type high-pressure apparatus. A mixture of crystalline Na₂Si₂O₅, V₂O₃ and SiO₂ was sealed in platinum capsules and maintained at 1773 K and 6 GPa for 20 h.

Crystal data

NaVSi ₂ O ₆	Mo K α radiation
$M_r = 226.10$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 22 reflections
$C2/c$	$\theta = 27.4\text{--}32.1^\circ$
$a = 9.6339 (4) \text{ \AA}$	$\mu = 2.85 \text{ mm}^{-1}$
$b = 8.7413 (2) \text{ \AA}$	$T = 296 \text{ K}$
$c = 5.2960 (3) \text{ \AA}$	Tablet
$\beta = 106.905 (2)^\circ$	$0.15 \times 0.12 \times 0.06 \text{ mm}$
$V = 426.72 (3) \text{ \AA}^3$	Green
$Z = 4$	
$D_x = 3.519 \text{ Mg m}^{-3}$	

Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{\max} = 40^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 17$
Absorption correction: by integration from crystal shape	$k = 0 \rightarrow 15$
$T_{\min} = 0.678$, $T_{\max} = 0.846$	$l = -9 \rightarrow 9$
1378 measured reflections	3 standard reflections monitored every 100 reflections for orientation and every 240 min for intensity
1378 independent reflections	intensity variation: -2.3%
1285 observed reflections [$I > 1.5\sigma(I)$]	

Refinement

Refinement on F	Extinction correction: isotropic secondary
$R = 0.017$	Extinction coefficient: 5.79×10^{-6}
$wR = 0.022$	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
$S = 0.8$	
1285 reflections	
48 parameters	
Unit weights applied (Δ/σ) _{max} < 0.005	
$\Delta\rho_{\max} = 0.539 \text{ e \AA}^{-3}$	
$\Delta\rho_{\min} = -0.630 \text{ e \AA}^{-3}$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_j$$

	x	y	z	U_{eq}
Na	0	0.30140 (9)	1/4	0.0120 (1)
V	0	0.90506 (3)	1/4	0.00385 (3)
Si	0.29177 (3)	0.09057 (3)	0.23925 (5)	0.00390 (4)
O1	0.11532 (8)	0.07946 (9)	0.1440 (1)	0.0053 (1)
O2	0.36103 (8)	0.25688 (9)	0.3054 (1)	0.0071 (1)
O3	0.35238 (8)	0.00921 (9)	0.0132 (1)	0.0067 (1)

Table 2. Geometric parameters (\AA , $^\circ$)

Atom labelling follows that of Clark, Appleman & Papike (1969).

Si tetrahedron		V octahedron	
Si—O1	1.629 (1)	V—O1A1,B1	2.058 (1)
Si—O2	1.595 (1)	V—O1A2,B2	2.064 (1)
Si—O3A1	1.639 (1)	V—O2C1,D1	1.946 (1)
Si—O3A2	1.648 (1)	Mean of 6	2.022
Mean of 4	1.628	O1A1—O1B1	2.765 (1)
O1—O2	2.750 (1)	O2C1—O2D1	2.903 (1)
O1—O3A1	2.644 (1)	O1A1—O2C1 $\times 2$	2.835 (1)
O1—O3A2	2.654 (1)	O1A1—O1A2 $\times 2$	2.990 (1)
O2—O3A1	2.648 (1)	O1A2—O2C1 $\times 2$	2.843 (1)
O2—O3A2	2.585 (1)	O1A2—O2D1 $\times 2$	2.951 (1)
O3A1—O3A2	2.653 (1)	O1A1—O1B2 $\times 2$	2.688 (1)
Si—Si	3.0853 (4)	V—V	3.1251 (2)
O1—Si—O2	117.02 (4)	O1A1—V—O1B1	84.41 (3)
O1—Si—O3A1	108.02 (4)	O1A1—V—O2C1 $\times 2$	90.13 (3)
O1—Si—O3A2	108.16 (4)	O1A1—V—O1A2 $\times 2$	93.02 (3)
O2—Si—O3A1	109.92 (5)	O1A1—V—O1B2 $\times 2$	81.39 (3)
O2—Si—O3A2	105.70 (4)	O1A2—V—O2C1 $\times 2$	90.25 (3)
O3A1—Si—O3A2	107.65 (4)	O1A2—V—O2D1 $\times 2$	94.75 (3)
		O2C1—V—O2D1	96.51 (4)
Na antiprism		Si—O3—Si	139.70 (5)
Na—O1A1,B1	2.382 (1)	V—O1—V	98.61 (3)
Na—O2C2,D2	2.401 (1)	O3—O3—O3	173.04 (4)
Na—O3C1,D1	2.420 (1)		
Na—O3C2,D2	2.804 (1)		
Mean of 8	2.502		

Table 3. Differences d_{br-mbr} (\AA) and O1—S1—O2 angles ($^\circ$) in $\text{NaM}^{3+}\text{Si}_2\text{O}_6$ pyroxenes

M^{3+}	d_{br-mbr}	O1—S1—O2	Reference
Sc	0.042	116.5 (1)	(a)
Sc	0.040	116.54 (5)	(b)
Cr	0.036	116.8 (2)	(c)
V	0.031	117.02 (4)	(d)
Ti	0.025	117.2 (2)	(e)
Al	0.019	118.5 (1)	(c)
In	0.040	115.2 (1)	(f)
In	0.042	115.07 (10)	(g)
Mn	0.030	116.35 (9)	(h)
Fe	0.028	116.4 (1)	(c)
Ga	0.017	116.67 (20)	(i)

References: (a) Hawthorne & Grundy (1973); (b) Ohashi, Osawa & Sato (1994); (c) Clark, Appleman & Papike (1969); (d) this work; (e) Ohashi, Fujita & Osawa (1982); (f) Hawthorne & Grundy (1974); (g) Ohashi, Osawa & Sato (1990); (h) Ohashi, Osawa & Tsukimura (1987); (i) Ohashi, Fujita & Osawa (1983).

The calculation was initiated with the atomic parameters of NaAlSi₂O₆ given by Clark, Appleman & Papike (1969). All calculations were performed with the SDP program system (B. A. Frenz & Associates, Inc., 1982).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: AS1073). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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l'Undecasulfure de Difer et d'Hexaytterbium, Fe₂Yb₆S₁₁

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Abstract

Two types of coordination polyhedra are present. The prismatic positions are occupied by Yb atoms. Yb and Fe atoms lie on octahedral sites with the same occupancy factor, and without any tendency to statistical disorder. Fe is divalent and Yb trivalent. The structure consists of prismatic rows along the *a* axis linked by ribbons of octahedral sites.

Commentaire

Ce travail s'inscrit dans l'étude des sulfures mixtes de métaux de transition du groupe 3d et de terres rares effectuée dans notre laboratoire tant par diffraction des rayons X sur monocristal que par microscopie électronique.

Une systématique des structures appartenant aux systèmes Mn–Yb–S (Bakker & Hyde, 1978) et Cr–Er–S (Tomas & Guittard, 1980) montre qu'elles se différencient par l'agencement de séquences 'O–P' et 'O–O–P' (O = octaèdre, P = prisme). Il nous a paru intéressant de généraliser ces résultats au

système FeS–Yb₂S₃ afin de comparer l'environnement des cations Fe²⁺, Mn²⁺ et Cr²⁺.

Le composé Fe₂Yb₆S₁₁ est obtenu à partir du mélange 0,25FeS + 0,75Yb₂S₃, chauffé à 1473 K durant trois heures dans un four à induction sous un courant de H₂S. Dans le but d'améliorer la qualité des cristaux, l'échantillon, disposé dans une ampoule scellée sous vide, est soumis à un recuit effectué à 1323 K durant 15 jours en présence de traces d'iode. Les cristaux utilisés pour la détermination structurale ont été extraits de cette préparation.

Les atomes d'Yb présentent deux types de polyèdres de coordination:

(1) Les sites Yb(1) et Yb(2) sont prismatiques à base triangulaire avec une septième liaison équatoriale légèrement plus longue que les précédentes. Dans ces deux sites, les distances moyennes du cation Yb³⁺ aux six atomes de S constituant le prisme valent 2,77 Å et correspondent sensiblement à la somme des rayons ioniques (Shannon, 1976): Yb³⁺(VII)—S² 2,76 Å. Relativement peu répandu dans les sulfures où l'Yb possède de préférence un environnement octaédrique, ce type de configuration se retrouve dans les composés CeYb₃S₆ (Rodier & Laruelle, 1973) et Mn_{2/3}Yb_{7/3}S₄ (Lemoine, Tomoas & Guittard, 1992) avec des distances du même ordre de grandeur (3,67–2,88 Å).

(2) Les atomes d'Yb partagent avec les atomes de Fe les sites octaédriques met(3), met(4) et met(5) avec le même taux d'occupation (0,6Yb³⁺ + 0,4Fe²⁺). La moyenne des distances métal–soufre (2,63 Å) est en bon accord avec celle obtenue en effectuant la somme des rayons ioniques. Ce type d'environnement mixte est habituellement rencontré pour ces éléments dans leurs sulfures avec des liaisons du même ordre: 2,612 Å dans Fe_{0,61}Yb_{0,26}S (Tomas, Palazzi, Chaqour, Guittard & Guymont, 1992), 2,707 Å dans FeYb₂S₄ (Tomas, Guittard & Brossard, 1980).

Cette structure peut être décrite comme constituée de colonnes de prismes à base triangulaire disposées parallèlement à l'axe *a* et reliées entre elles par des rubans plans d'octaèdres. Si les symboles 'O' et 'P' représentent respectivement un octaèdre et un prisme et *M* un atome de Fe ou d'Yb, cet enchaînement correspond au motif (O–P–P)₂–(O–P) et à la formule chimique M₈S₁₁. Nous retrouvons les caractéristiques des structures rencontrées lors de l'étude des systèmes MnS–Yb₂S₃ (Bakker & Hyde, 1978) et CrS–Er₂S₃ (Tomas & Guittard, 1980). Les cations Fe²⁺ jouent le même rôle que ceux de Mn²⁺ et partagent le site octaédrique régulier du cation trivalent de terre rare. Ils se différencient donc de Cr²⁺ qui, dans le composé CrEr₂S₄ (Tomas, Chevalier, Laruelle & Bachet, 1976), occupe des sites octaédriques propres dont la déformation est attribuée à l'effet Jahn–Teller que présente le Cr divalent en