data with both normal and non-normal senses of the anomalous-dispersion effect (Stout & Jensen, 1989). For the non-normal sense $R = 0.0249$ and $wR = 0.0453$, whereas for the normal sense $R = 0.0147$ and $wR = 0.0249$. In separate calculations, *SHELXL* (Sheldrick, 1994) was used to refine the Flack x parameter (Flack, 1983; Bernardinelli & Flack, 1985) simultaneously with the coordinates and yielded the value $x = 0.037$ (20). These results demonstrate decisively that the space-group assignment and the coordinates (as given in Table 1) have been chosen correctly, determining the absolute structure.

The positional and displacement parameters for the water molecule are uncertain. One analysis places the water O atom, O(5), at a special position $(x, 0, \frac{1}{3})$ whereupon its B_{eq} refines to a value almost four times the corresponding mean value for the sulfate O atoms O(1)-O(4); its U_{33} is almost ten times the corresponding mean value for the sulfate O atoms. An alternative analysis, adopted for this report, involves disordering O(5) by moving it with half-occupancy 0.28 Å from the special position given above (see Fig. 2). The final B_{eq} value for O(5) in this second model is approximately 1.8 times the corresponding mean value for the sulfate O atoms. For the final refinement cycles, a water H atom, H, was assigned to a fixed position obtained from a difference Fourier map with an isotropic displacement parameter fixed at 1.5 times B_{eq} of O(5). It should be noted that all these variations in O(5) and H assignments produced very small effects on any of the other atoms; for example, the average maximum change in the positional parameters of the sulfate O atoms was only 1.3 times the corresponding e.s.d.'s.

The maximum positive residual electron density (1.02 e Å^{-3}) occurred 0.29 Å from Na while the next highest (0.42 e Å^{-3}) occurred 0.43 Å from O(2); the maximum negative peak (−0.42 e Å^{-3}) occurred 0.65 Å from S.

Rigid-body analysis of the Na-O polyhedron, the La-O polyhedron and the sulfate ion was performed using the program *THMA*11 (Trueblood, 1986) which is based on the work of Schomaker & Trueblood (1968). Neither the Na-O nor the La-O polyhedron conformed to rigid-body behavior, but the sulfate ion did; the average magnitude of the differences in the mean-square displacement amplitudes along the interatomic vectors for the ten unique atom pairs of the sulfate ion was 15 (16) × 10^{-4} Å^2. The Hirshfeld (1976) rigid-bond test, extended as described by Rosenfield, Trueblood & Dunitz (1978), is satisfied and the corrected S—O bond lengths are given in Table 2.

Owing to the lack of a single definitive interpretation of the water molecule geometry (as described above), the water H-atom position is reported as found but has not been adjusted to account for the usual foreshortening of O—H distances observed in X-ray determinations.

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$NaScSi_2O_6$

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Abstract

The structure of $NaScSi_2O_6$ pyroxene formed at 6 GPa pressure, is isomorphous with that of $NaScSi_2O_6$ formed at atmospheric pressure. However, the cell parameters and the atomic coordinates are different. The $NaScSi_2O_6$ pyroxene obtained by the quenching method is sluggish in changing structure and the structure obtained is not always that of the equilibrium state at room temperature and atmospheric pressure.

Comment

The structure of $NaScSi_2O_6$ pyroxene synthesized at atmospheric pressure (Ito & Frondel, 1968) was determined by Hawthorne & Grundy (1973). Cell parameters of the $Na(Sc,In)Si_2O_6$ pyroxenes formed at 6 GPa pressure show approximately linear relationships {*e.g.* $b = -0.0777[Sc/(Sc+In)]+9.131$ Å} with chemical composition (Ohashi, Osawa & Sato, 1990). Cell parameters of the $NaScSi_2O_6$ pyroxene synthesized at atmospheric pressure (Hawthorne & Grundy, 1973) deviate significantly from the above trend. On the other hand, the cell parameters of the $NaScSi_2O_6$ pyroxene formed at 6 GPa pressure are very similar to values extrapolated from the $Na(Sc,In)Si_2O_6$ pyroxenes formed at 6 GPa pressure.

The atomic coordinates [$y = 0.89627$ (6) for Sc, $z = 0.2439$ (1) for Si and $z = 0.0179$ (3) for O3] of the $NaScSi_2O_6$ pyroxene formed at atmospheric pressure differ from those of the $NaScSi_2O_6$ pyroxene formed at 6 GPa pressure. However, selected interatomic distances and angles are very similar. Different synthetic conditions give different cell parameters and atomic coordinates for $NaScSi_2O_6$ pyroxene. This fact means that the $NaScSi_2O_6$ pyroxene obtained by the quenching method is sluggish in changing structure and that the structure is not always that of the equilibrium state at room temperature and atmospheric pressure.

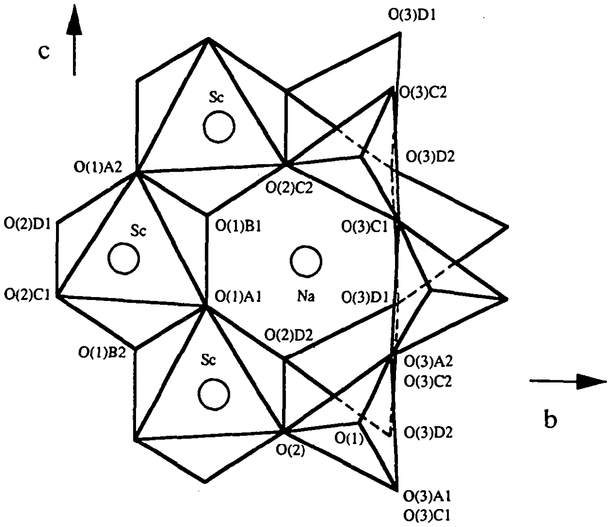

Fig. 1. a^*-axis projection of $NaScSi_2O_6$. Atom nomenclature follows that used by Clark, Appleman & Papike (1969).

Experimental

The title compound was prepared by solid-state reaction using belt-type high-pressure apparatus. A mixture of crystalline $Na_2Si_2O_5$, Sc_2O_3 and SiO_2 was sealed in a platinum capsule and maintained at 1773 K and 6 GPa for 20 h.

Crystal data

$NaScSi_2O_6$
$M_r = 220.11$
Monoclinic
$C2/c$
$a = 9.8372$ (10) Å
$b = 9.0550$ (5) Å
$c = 5.3488$ (6) Å
$\beta = 107.175$ (5)°
$V = 455.21$ (7) Å^3
$Z = 4$
$D_x = 3.21$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 26.4$-31.3°
$\mu = 2.18$ mm^{-1}
$T = 298$ K
Prism
$0.08 \times 0.05 \times 0.04$ mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω-2θ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.895$, $T_{\max} = 0.921$
1047 measured reflections
1047 independent reflections
895 observed reflections [$I > 1.5\sigma(I)$]
$\theta_{\max} = 35$°
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 14$
$l = -8 \rightarrow 8$
3 standard reflections monitored every 100 reflections for orientation and every 240 min for intensity
intensity variation: -1.9%

Refinement

Refinement on F
$R = 0.018$
$wR = 0.034$
$S = 1.3$
895 reflections
48 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} < 0.005$
$\Delta\rho_{\max} = 0.4$ e Å^{-3}
$\Delta\rho_{\min} = -0.4$ e Å^{-3}
Extinction correction: isotropic secondary
Extinction coefficient: 1.34×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Na	0	0.3036 (1)	1/4	0.0166 (2)
Sc	0	0.89607 (4)	1/4	0.00466 (6)
Si	0.29126 (4)	0.08712 (4)	0.24447 (7)	0.00466 (7)
O(1)	0.1182 (1)	0.0781 (1)	0.1458 (2)	0.0060 (2)
O(2)	0.3592 (1)	0.2477 (1)	0.3073 (2)	0.0081 (2)
O(3)	0.3503 (1)	0.0081 (1)	0.0188 (2)	0.0076 (2)

Table 2. *Selected geometric parameters* (Å, °)

Si tetrahedron		Sc octahedron	
Si—O(1)	1.628 (1)	Sc—O(1)*A*1,*B*1	2.183 (1)
Si—O(2)	1.594 (1)	Sc—O(1)*A*2,*B*2	2.106 (1)
Si—O(3)*A*1	1.650 (1)	Sc—O(2)*C*1,*D*1	2.017 (1)
Si—O(3)*A*2	1.652 (1)	Mean	2.102
Mean	1.631		
Si—Si	3.1051 (5)	Sc—Sc	3.2703 (3)
Na antiprism			
Na—O(1)*A*1,*B*1	2.493 (1)	Si—O(3)—Si	140.24 (6)
Na—O(2)*C*2,*D*2	2.409 (1)	Sc—O(1)—Sc	99.37 (4)

Na—O(3)*C*1,*D*1	2.460 (1)	O(3)—O(3)—O(3)	173.74 (5)
Na—O(3)*C*2,*D*2	2.897 (1)		
Mean	2.565		

All calculations were performed using the *SDP* system of programs (B. A. Frenz & Associates, Inc., 1985).

Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71625 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1046]

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CdV$_2$(P$_2$O$_7$)$_2$

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Abstract

Cadmium vanadium diphosphate, CdV$_2$(P$_2$O$_7$)$_2$, is isotypic with AV$_2$(P$_2$O$_7$)$_2$ (A = Ca, Sr) and Na$_x$MoP$_2$O$_7$ ($0.25 < x < 0.50$). Its structure consists of similar [VP$_4$O$_{14}$]$_\infty$ columns which are built up from VO$_6$ octahedra and P$_2$O$_7$ pyrophosphate groups, and linked together through VO$_6$ octahedra. This framework delimits tunnels in which the Cd ions are located with octahedral coordination. A comparison with AV$_2$(P$_2$O$_7$)$_2$ (A = Ca, Sr) is given.

Comment

The studies performed over the past few years on diphosphates of transition elements with the formula A_xMP$_2$O$_7$ have allowed three diphosphates with very similar [M_2P$_4$O$_{14}$]$_\infty$ frameworks to be isolated: the vanadium diphosphates AV$_2$(P$_2$O$_7$)$_2$ (A = Ca, Sr; Hwu & Willis, 1991) and the molybdenum diphosphate Na$_x$MoP$_2$O$_7$ ($0.25 \leq x \leq 0.50$; Leclaire, Borel, Grandin & Raveau, 1988). The stability of this structure type seems to be governed mainly by the size of the A cation since the vanadium diphosphate BaV$_2$(P$_2$O$_7$)$_2$ (Benhamada, Grandin, Borel, Leclaire & Raveau, 1991) exhibits a very different structure. In order to understand this behaviour, it is necessary to substitute the A cations with cadmium whose size is smaller than calcium and sodium. We report here the crystal structure of a new diphosphate, CdV$_2$(P$_2$O$_7$)$_2$, which is isotypic with SrV$_2$(P$_2$O$_7$)$_2$.

This new cadmium vanadium(III) phosphate exhibits the SrV$_2$(P$_2$O$_7$)$_2$-type structure. Its [V$_2$P$_4$O$_{14}$]$_\infty$ framework consists of similar VP$_4$O$_{16}$ units built up from VO$_6$ octahedra linked in a *trans* configuration to two bidentate P$_2$O$_7$ groups. These VP$_4$O$_{16}$ units are linked together forming [VP$_4$O$_{14}$]$_\infty$ columns, running along **a**, which are connected through VO$_6$ octahedra (Fig. 1). The [V$_2$P$_4$O$_{14}$]$_\infty$ framework delimits two types of tunnel: small empty tunnels and larger ones where Cd ions are located. In the series AV$_2$(P$_2$O$_7$)$_2$, the cell parameters decrease with the size of the A cation, *i.e.* $\mathrm{Sr}^{2+} > \mathrm{Ca}^{2+} > \mathrm{Cd}^{2+}$. The PO$_4$ tetrahedra in CdV$_2$(P$_2$O$_7$)$_2$ exhibit a geometry and interatomic distances (Table 2) similar to those observed in SrV$_2$(P$_2$O$_7$)$_2$.

The VO$_6$ octahedra are significantly more distorted (Table 2) than those in the Sr diphosphate. Indeed, one observes V—O distances ranging from 1.94 to 2.149 Å for Cd, whereas they vary from 1.95 to 2.09 Å for Sr. In the same way, the O···O distances range from 2.643 to 3.130 Å in the Cd phase compared with 2.724 to 2.914 Å in the Sr phase, and the O—V—O angles extend from 81.0 to 99° for Cd as opposed to 86.94 to 92.27° for Sr.

An interesting structural feature concerns the Cd-ion coordination which can be described as slightly distorted octahedral with six Cd···O distances

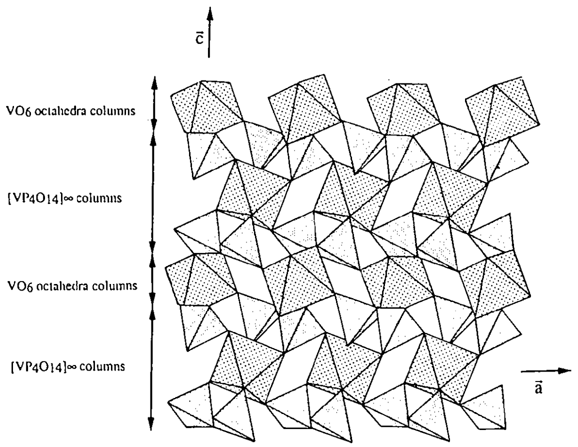

Fig. 1. Projection of the structure along **b**.