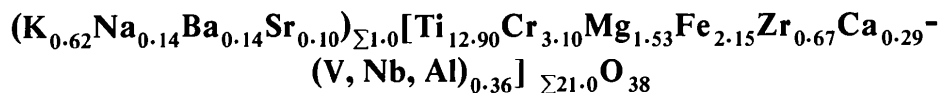


## Structure Refinement of Mathiasite,



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(Received 24 September 1982; accepted 15 December 1982)

**Abstract.**  $M_r = 1693.08$ , rhombohedral,  $R\bar{3}$ ,  $a = 9.119(3) \text{ \AA}$ ,  $\alpha = 69.24(2)^\circ$ ,  $Z = 1$ ,  $D_x = 4.39 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$ ,  $\mu = 68.8 \text{ cm}^{-1}$ . Final  $R = 0.054$  for 892 observed unique diffractometer data. Mathiasite is isostructural with the crichtonite-group minerals,  $AM_{21}O_{38}$ , and is characterized by dominant potassium in the large-cation  $A$  site. Partial disorder in the  $M$ -cation sublattice is interpreted as due to the partial occupation of a second anion site by large cations.

**Introduction.** New rhombohedral Ba–Sr–K–Cr–Fe titanate minerals, related to the crichtonite-group minerals (Gatehouse, Grey, Campbell & Kelly, 1978), have been recently identified in peridotite nodules from the Bultfontein kimberlite in South Africa (Smyth, Erlank & Rickard, 1978). The compositions conform to the general formula  $AM_{21}O_{38}$ ,  $A$  = large cations (occupying a 12-coordinate anion site in crichtonite) and  $M$  = small cations. Two new members, with  $A$  = dominant Ba and K have been provisionally named lindsleyite and mathiasite respectively. In this paper we report the structure refinement for the K-dominant member, mathiasite.

Electron microprobe analyses (average of three points) gave Ti, 36.7; Cr, 9.58; Fe, 7.17; Zr, 3.65; Mg, 2.21; K, 1.44; Ba, 1.16; Ca, 0.69; Sr, 0.52; Nb, 0.55; V, 0.39; Al, 0.18, Na, 0.18 wt%. The corresponding unit-cell composition, normalized to 38 oxygens, and with the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio adjusted to give 22 cations is:  $(\text{K}_{0.62}\text{Na}_{0.14}\text{Ba}_{0.14}\text{Sr}_{0.10})[\text{Ti}_{12.90}\text{Cr}_{3.10}\text{Mg}_{1.53}\text{Fe}_{2.15}\text{Zr}_{0.67}\text{Ca}_{0.29}(\text{V}, \text{Nb}, \text{Al})_{0.36}]\text{O}_{38}$  i.e.  $AM_{21}O_{38}$  with  $A$  = large cations, K, Na, Ba, Sr.

**Experimental.** Crystal fragment measuring  $0.044 \times$

$0.069 \times 0.125 \text{ mm}$  used for intensity data collection, PW1100 automated four-circle diffractometer, graphite-monochromated Mo  $K\alpha$ ,  $\omega-2\theta$  scans,  $\theta$  range  $3-30^\circ$ , scan speed  $0.05^\circ \text{ s}^{-1}$ , variable scan width  $\Delta\theta = (1.20 + 0.3 \tan \theta)^\circ$ ; lattice parameters obtained from average of 15 orientation matrices from data collection; data corrected for absorption, maximum and minimum transmission factors 0.705 and 0.323; 5027 ( $\pm h, k, l$ ) reflections collected and reduced to 1251 unique reflections, of which 892 with  $I > 3\sigma(I)$  used in the refinement; atomic coordinates for loweringite (Gatehouse *et al.*, 1978) in space group  $R\bar{3}$  used as starting parameters, and the cations ordered into sites  $M(0)-M(5)$  in order of decreasing size, as found for other crichtonite-group minerals; full-matrix least-squares refinement of the scale factor, positional and isotropic thermal parameters converged at  $R = 0.06$ .

The temperature factor for O(7) was almost zero and a difference Fourier map revealed a subsidiary peak at 0.37, 0.37, 0.37, of height  $3 \text{ e \AA}^{-3}$ . Bond-length calculations confirmed that this corresponded to an octahedrally coordinated atom,  $\overline{M-O} = 2.12 \text{ \AA}$ , which face-shared to the  $M(2)$  tetrahedron on the trigonal axis. This site,  $M(6)$ , was allowed partial occupancy by Mg and a corresponding reduction in the site occupancy of  $M(2)$  was introduced. The population parameters for  $M(6)$  and O(7) were refined and finally, a refinement of all coordinates and isotropic thermal parameters was carried out, resulting in convergence at  $R = 0.054$ ,  $R_w = 0.045$  [ $w = 1/\sigma^2(F)$ ] for the observed reflections.

Scattering factors for neutral atoms were those of Cromer & Mann (1968), anomalous-dispersion corrections for all atoms from Cromer & Liberman (1970); *SHELX* 76 (Sheldrick, 1976) and *XRAY* 76 (Stewart, 1976) programs were used for all computing.

**Discussion.** Final positional and isotropic temperature factors are given in Table 1.\* Bond lengths associated with the different polyhedra are given in Table 2.

\* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38283 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and isotropic thermal parameters*

	Occupancy	x	y'	z	B(Å <sup>2</sup> )
M(0)	0.62 K + 0.14Na + 0.14Ba + 0.10Sr	0	0	0	1.24 (6)
M(1)	0.7 Zr + 0.3 Ca	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.26 (3)
M(2)	0.9 Mg + 0.9 Fe	0.3111 (1)	0.3111 (1)	0.3111 (1)	0.36 (5)
M(3)	0.9 Ti + 3.1 Cr + 1.3 Fe + 0.7 (V,Nb,Mg)	0.3479 (2)	0.1227 (2)	0.0232 (2)	0.58 (2)
M(4)	6 Ti	0.3071 (2)	0.7208 (2)	0.1457 (2)	0.38 (2)
M(5)	6 Ti	0.4754 (2)	0.0832 (2)	0.6386 (2)	0.38 (2)
M(6)	0.2 Mg	0.3692 (26)	0.3692 (26)	0.3692 (26)	2.23 (1.19)
O(1)		0.3084 (7)	0.6261 (7)	0.3820 (7)	0.52 (9)
O(2)		0.1553 (7)	0.2394 (7)	0.9392 (6)	0.52 (9)
O(3)		0.9218 (7)	0.4583 (7)	0.2979 (7)	0.52 (8)
O(4)		0.1424 (7)	0.5175 (7)	0.9902 (7)	0.52 (8)
O(5)		0.3901 (7)	0.4879 (7)	0.1343 (7)	0.37 (8)
O(6)		0.7043 (6)	0.2434 (7)	0.0743 (7)	0.42 (8)
O(7)	PP = 1.056 (18)	0.2133 (3)	0.2133 (3)	0.2133 (3)	0.45 (14)

Table 2. *M—O bond lengths (Å)*

M(0) cuboctahedron		M(4) octahedron (titanium)	
M(0)—O(2) × 6	2.803 (7)	M(4)—O(2)	1.889 (6)
M(0)—O(6) × 6	2.861 (5)	M(4)—O(6)	1.949 (7)
Mean	2.832	M(4)—O(3)	1.967 (6)
		M(4)—O(5)	2.014 (6)
M(1) octahedron		M(4)—O(1)	2.020 (6)
M(1)—O(1) × 6	2.136 (6)	M(4)—O(6)'	2.028 (6)
		Mean	1.978
M(2) tetrahedron		M(5) octahedron (titanium)	
M(2)—O(5) × 3	1.969 (6)	M(5)—O(4)	1.885 (7)
M(2)—O(7)	2.019 (4)	M(5)—O(1)	1.902 (6)
Mean	1.981	M(5)—O(3)	1.930 (6)
		M(5)—O(5)	1.987 (7)
M(3) octahedron		M(5)—O(6)	2.007 (7)
M(3)—O(4)	1.934 (6)	M(5)—O(5)'	2.114 (8)
M(3)—O(3)	1.963 (7)	Mean	1.971
M(3)—O(2)	1.963 (6)		
M(3)—O(4)'	1.992 (6)	M(6) octahedron	
M(3)—O(7)	1.995 (3)	M(6)—O(5) × 3	2.003 (20)
M(3)—O(2)'	2.032 (6)	M(6)—O(1) + 3	2.244 (25)
Mean	1.980	Mean	2.123

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*Acta Cryst.* (1983). C39, 422–425

## Tetradecapraseodymium Hexanickel Undecasilicide, Pr<sub>14</sub>Ni<sub>6</sub>Si<sub>11</sub>, with Centered Trigonal Rare-Earth Prisms

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(Received 18 October 1982; accepted 1 December 1982)

**Abstract.**  $M_r = 2634$ , monoclinic,  $C2/m$ ,  $a = 113.72(1)^\circ$ ,  $V = 2809.7 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 33.991(3)$ ,  $b = 4.2328(4)$ ,  $c = 21.330(3) \text{ \AA}$ ,  $\beta = 6.226 \text{ Mg m}^{-3}$ ,  $\text{Mo K}\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu =$

0108-2701/83/040422-04\$01.50

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