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The Crystal Structure of Nambulite (Li,Na)Mn₄Si₅O₁₄(OH)

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Nambulite, (Li,Na)Mn₄Si₅O₁₄(OH), is triclinic with $a=7.621$ (5), $b=11.761$ (8), $c=6.731$ (5) Å, $\alpha=92^\circ 46$ (3)', $\beta=95^\circ 05$ (3)', $\gamma=106^\circ 52$ (5)' and $D_x=3.55$ g cm⁻³. The space group is $P\bar{1}$ and $Z=2$. The crystal structure has been determined by the Patterson method and refined to an R value of 0.086 for all 2233 reflexions collected by the counter method. The structure consists of infinite silicate chains with a repeat unit of five tetrahedra, and Mn polyhedral bands, both parallel to [110]. The mean Mn–O distances are 2.233, 2.242, 2.188 and 2.410 Å for crystallographically independent Mn polyhedra. The mean (Li,Na)–O distance is 2.487 Å for (Li,Na) polyhedra. The mean Si–O distances are 1.621, 1.623, 1.623, 1.626 and 1.630 Å for independent Si tetrahedra. In spite of the difference in the number of cations, nambulite is more closely related to baringtonite, Ca₂Fe²⁺Fe³⁺Si₅O₁₄(OH), than to rhodonite, CaMn₄Si₅O₁₅, in the arrangement of silicate chains and polyhedral bands.

Introduction

Nambulite is a new mineral with the ideal formula LiNaMn₈Si₁₀O₂₈(OH)₂ (Yoshii, Aoki & Maeda, 1972). Because of the similarity of the cell dimensions and chemical composition of nambulite and rhodonite, CaMn₄Si₅O₁₅ (Liebau, Hilmer & Lindemann, 1959; Peacor & Niizeki, 1963), Yoshii *et al.* (1972) considered that both minerals should have essentially the same crystal structure. However, they suspected that Li and Na atoms might occupy independent positions in the structure of nambulite, because of the difference in the ionic radii of Li and Na atoms. In a study of the crystal chemistry of the system Li₂SiO₃–Mn₂SiO₄–SiO₂–H₂O, Ito (1972) reported that the maximum substitution of Na for Li in synthetic hydrorhodonite, LiMn₄Si₅O₁₄(OH), did not exceed 30% of the total Li.

Nambulite also has some similarity in cell dimensions and chemical composition to babingtonite, Ca₂Fe²⁺Fe³⁺Si₅O₁₄(OH), though the numbers and species of large cations in the two minerals are different. The structure of babingtonite has been determined by Araki & Zoltai (1972) and found to have the *Fünferketten pyroxenoid structure*.

In this investigation the crystal structure of nambulite has been studied to determine the arrangement of Li and Na atoms in the structure, and to elucidate the structural relationships between nambulite, rhodonite and babingtonite.

Experimental

Single crystals of nambulite from the Funakozawa Mine, Iwate, Japan, were used in this study. They are triclinic. The cell dimensions, obtained with a four-

circle diffractometer (Mo $K\alpha_1$, $\lambda=0.70926$ Å), are $a=7.621$ (5), $b=11.761$ (8), $c=6.731$ (5) Å, $\alpha=92^\circ 46$ (3)', $\beta=95^\circ 05$ (3)' and $\gamma=106^\circ 52$ (5)'. These values are in agreement with those of Yoshii *et al.* (1972). The estimated standard deviations of the cell dimensions were obtained from the relative errors derived from the equation $2d \sin \theta = n\lambda$ by considering possible errors in the measurement of angles. The space group was determined to be $P\bar{1}$ by the $N(z)$ test (Howells, Phillips & Rogers, 1950) and this was confirmed by the structure determination.

The single crystal used for the data collection was a plate of dimensions $0.003 \times 0.006 \times 0.009$ cm. 2233 independent reflexions were measured on the four-circle diffractometer by the ω - 2θ scan technique within the range $(\sin \theta)/\lambda \leq 0.60$. Mo $K\alpha$ radiation was used. Data reduction was made in the usual way by applying Lorentz and polarization factors. No absorption correction was made.

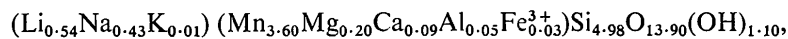
Structure determination and refinement

A three-dimensional Patterson map of nambulite revealed that strong peaks representing the Mn–Mn vectors are arranged in almost the same way as in the maps for rhodonite and babingtonite. Because nambulite and rhodonite both contain five cations besides

out as follows. First, we assumed that nambulite had the ideal chemical composition and that Li and Na atoms occupied the M(5) site in complete disorder. Several cycles of least-squares refinements were carried out varying the atomic coordinates, individual isotropic temperature factors and one scale factor. The program *ORFLS* of Busing, Martin & Levy (1962), modified by Sakurai (1967) to the UNICS was used in all refinements. The function minimized was $\sum 1/\sigma^2 ||F_o| - k|F_c||^2$, where σ represents the estimated standard deviation computed from counting statistics and k is a scale factor. Scattering factors for Mn^{2+} and Si^{4+} were taken from *International Tables for X-ray Crystallography* (1962), and that for O^{2+} from Tokonami (1965). Two cycles were carried out varying the isotropic temperature factors and the multiplicities of the five independent cations. The multiplicities are 1.020 (4), 1.037 (3), 1.026 (4), 1.033 (4) for Mn atoms in the M(1), M(2), M(3) and M(4) sites, respectively, and 0.687 (7) for Na atoms in the M(5) site.

These values indicate that all the cation sites are occupied by Mn atoms except for the M(5) site. The multiplicity for the M(5) site is close to the value 0.636 corresponding to an occupancy 0.5Li and 0.5Na.

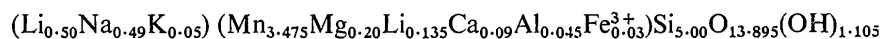
At this stage of the investigation, one of the authors (M.Y.) redetermined the chemical composition of nambulite. The new chemical composition is



the Si and H atoms in the asymmetric unit, the structure of rhodonite determined by Peacor & Niizeki (1963) was used as an initial structure for nambulite and refined by successive Fourier syntheses and the least-squares method. However, the value of R did not drop below 0.32 for all reflexions.

Further study of the Patterson map of nambulite indicated that the arrangement of peaks corresponding to the vectors between Si and Mn atoms is more like that of babingtonite than that of rhodonite. Because babingtonite contains only four (Ca, Fe) atoms in an asymmetric unit, the coordinates for the four atoms obtained by Araki & Zoltai (1972) were used as initial values. By successive Fourier and difference syntheses we have succeeded in finding an additional site for Li and Na atoms which is absent in babingtonite.

At this stage of the structure analysis the chemical composition



given by Yoshii *et al.* (1972) was adopted by using appropriate atomic scattering factors. However, in the difference syntheses positive peaks were always observed at the Mn sites, suggesting that the above chemical composition did not necessarily represent the composition of the fragment used in the present investigation. The refinements were, therefore, carried

which is close to the ideal composition of $(Li_{0.5}Na_{0.5})Mn_4Si_5O_{14}(OH)$ obtained by the structure analysis. The calculated density is 3.55 g cm $^{-3}$. In the final cycle the atomic coordinates and isotropic temperature factors of the Mn atoms at the sites M(1) to M(4) and those of $(Li + Na)/2$ at M(5) were refined together with one scale factor. The maximum shift in atomic parameters in the last cycle was less than 0.10 times the corresponding standard deviation. The final R and weighted R are 0.086 and 0.041 respectively for all 2233 reflexions. Refinement with anisotropic temperature factors was not carried out. Further refinement based on the space group $P1$ with the ordered distribution of Li and Na atoms resulted in larger estimated standard deviations in the atomic coordinates without any improvement in the R value.

The final atomic coordinates and individual isotropic temperature factors with estimated standard deviations are given in Table 1. Selected interatomic

distances and angles for nambulite are given in Table 2.* All computations were carried out at the Computa-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31056 (16 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates and isotropic temperature factors (except for those of the hydrogen atom)

The standard deviations are given in parentheses in the unit of the last digit.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> [Å ²]
M(1)	0.5912 (2)	0.6514 (1)	0.0631 (2)	0.26 (2)
M(2)	0.8103 (2)	0.9417 (1)	0.1258 (2)	0.28 (2)
M(3)	0.0407 (2)	0.2354 (1)	0.1759 (2)	0.49 (3)
M(4)	0.2433 (2)	0.5143 (1)	0.2645 (1)	0.76 (3)
M(5)	0.6751 (2)	0.1432 (1)	0.3681 (2)	1.16 (9)
Si(1)	0.2720 (3)	0.0599 (2)	0.3592 (4)	0.91 (4)
Si(2)	0.4698 (3)	0.3291 (2)	0.4275 (4)	0.92 (4)
Si(3)	0.8152 (3)	0.4539 (2)	0.2202 (4)	0.87 (4)
Si(4)	0.0008 (3)	0.7244 (2)	0.3034 (4)	0.82 (4)
Si(5)	0.3454 (3)	0.8545 (2)	0.1203 (4)	0.94 (4)
O(1)	0.1880 (8)	0.0074 (5)	0.5595 (8)	1.37 (11)
O(2)	0.1197 (8)	0.0669 (5)	0.1845 (8)	0.95 (11)
O(3)	0.4254 (8)	0.1847 (5)	0.4257 (8)	1.55 (11)
O(4)	0.3276 (8)	0.3521 (5)	0.2517 (9)	1.12 (12)
O(5)	0.5379 (8)	0.6123 (5)	0.3542 (8)	1.19 (11)
O(6)	0.6878 (8)	0.3757 (5)	0.3806 (8)	1.10 (11)
O(7)	0.9767 (8)	0.3973 (5)	0.1736 (9)	1.36 (12)
O(8)	0.6812 (8)	0.4695 (5)	0.0341 (8)	1.03 (11)
O(9)	0.9246 (8)	0.5832 (5)	0.3399 (8)	1.17 (11)
O(10)	0.8758 (8)	0.7658 (5)	0.1325 (8)	1.07 (11)
O(11)	-0.0138 (8)	0.2042 (5)	0.4830 (9)	1.28 (11)
O(12)	0.2109 (8)	0.7451 (5)	0.2357 (9)	1.36 (11)
O(13)	0.5313 (8)	0.8243 (5)	0.0776 (9)	1.11 (11)
O(14)	0.7675 (8)	0.1196 (5)	0.0748 (8)	1.15 (11)
O(15)	0.3935 (8)	0.9729 (5)	0.2811 (8)	1.07 (11)

tion Center of Osaka University using the UNICS system (Sakurai, 1967).

Description of the structure and discussion

The structure of nambulite is shown projected along *c* in Fig. 1, and normal to (111), which is parallel to

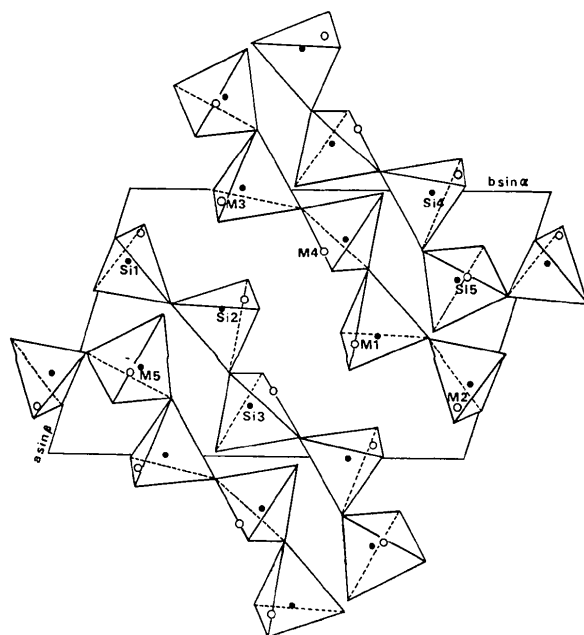


Fig. 1. The structure of nambulite projected along the *c* axis.

Table 2. Selected bond distances (Å) and angles (°) of nambulite

The standard deviations are given in parentheses in the unit of the last digit.

M(1) octahedron		M(4) polyhedron	
M(1)-O(4)	2.273 (5)	M(4)-O(4)	2.176 (6)
M(1)-O(5)	2.112 (5)	M(4)-O(5)	2.162 (5)
M(1)-O(8)	2.459 (6)	M(4)-O(6)	2.602 (5)
M(1)-O(8')	2.196 (5)	M(4)-O(7)	2.126 (5)
M(1)-O(10)	2.191 (5)	M(4)-O(8)	2.146 (5)
M(1)-O(13)	2.172 (6)	M(4)-O(9)	2.851 (6)
Average	2.233	M(4)-O(12)	2.805 (5)
		Average	2.410
M(2) octahedron		M(5) polyhedron	
M(2)-O(1)	2.174 (5)	M(5)-O(1)	2.338 (8)
M(2)-O(2)	2.391 (5)	M(5)-O(3)	2.155 (8)
M(2)-O(2')	2.215 (6)	M(5)-O(6)	2.707 (7)
M(2)-O(10)	2.262 (6)	M(5)-O(11)	2.320 (7)
M(2)-O(13)	2.174 (5)	M(5)-O(12)	2.867 (6)
M(2)-O(14)	2.239 (6)	M(5)-O(14)	2.200 (7)
Average	2.242	M(5)-O(15)	2.494 (7)
		M(5)-O(15')	2.795 (7)
		Average	2.485
		Shortest six	2.369
M(3) octahedron			
M(3)-O(2)	2.228 (4)	O(1)-O(2)	2.683 (7)
M(3)-O(4)	2.232 (6)	O(1)-O(3)	2.615 (7)
M(3)-O(7)	2.093 (7)	O(1)-O(15)	2.651 (8)
M(3)-O(10)	2.234 (7)	O(2)-O(3)	2.689 (7)
M(3)-O(11)	2.175 (6)	O(2)-O(15)	2.653 (8)
M(3)-O(14)	2.170 (5)	O(3)-O(15)	2.576 (9)
Average	2.188	Average	2.643
Si(1) tetrahedron			
Si(1)-O(1)	1.624 (6)	O(3)-O(4)	2.571 (9)
Si(1)-O(2)	1.585 (6)	O(3)-O(5)	2.677 (8)
Si(1)-O(3)	1.616 (5)	O(3)-O(6)	2.609 (7)
Si(1)-O(15)	1.661 (7)	O(4)-O(5)	2.731 (7)
Average	1.621	O(4)-O(6)	2.723 (8)
		O(6)-O(5)	2.570 (8)
		Average	2.647
Si(2) tetrahedron			
Si(2)-O(3)	1.635 (6)	O(6)-O(7)	2.684 (8)
Si(2)-O(4)	1.602 (6)	O(6)-O(8)	2.621 (8)
Si(2)-O(5)	1.593 (6)	O(6)-O(9)	2.647 (7)
Si(2)-O(6)	1.664 (6)	O(7)-O(8)	2.713 (9)
Average	1.623	O(7)-O(9)	2.564 (9)
		O(8)-O(9)	2.662 (7)
		Average	2.648
Si(3) tetrahedron			
Si(3)-O(6)	1.659 (6)	O(9)-O(10)	2.690 (8)
Si(3)-O(7)	1.604 (7)	O(9)-O(11)	2.603 (8)
Si(3)-O(8)	1.583 (6)	O(9)-O(12)	2.642 (7)
Si(3)-O(9)	1.649 (5)	O(10)-O(11)	2.660 (7)
Average	1.623	O(10)-O(12)	2.655 (8)
		O(12)-O(11)	2.684 (8)
		Average	2.655
Si(4) tetrahedron			
Si(4)-O(9)	1.633 (6)	O(12)-O(13)	2.702 (8)
Si(4)-O(10)	1.593 (6)	O(12)-O(14)	2.662 (8)
Si(4)-O(11)	1.614 (6)	O(12)-O(15)	2.642 (8)
Si(4)-O(12)	1.667 (6)	O(13)-O(14)	2.660 (9)
Average	1.626	O(13)-O(15)	2.678 (9)
		O(15)-O(14)	2.620 (7)
		Average	2.660
Si(5) tetrahedron			
Si(5)-O(12)	1.676 (6)		
Si(5)-O(13)	1.604 (7)		
Si(5)-O(14)	1.580 (6)		
Si(5)-O(15)	1.662 (6)		
Average	1.630		

Table 2 (cont)

O(1)—Si(1)—O(2)	113.4 (3)	O(9)—Si(3)—O(7)	104.0 (3)
O(1)—Si(1)—O(3)	107.6 (3)	O(9)—Si(4)—O(10)	112.9 (3)
O(1)—Si(1)—O(15)	107.6 (3)	O(9)—Si(4)—O(11)	106.5 (3)
O(2)—Si(1)—O(3)	114.3 (3)	O(9)—Si(4)—O(12)	106.3 (3)
O(2)—Si(1)—O(15)	109.6 (3)	O(10)—Si(4)—O(11)	112.1 (3)
O(3)—Si(1)—O(15)	103.6 (3)	O(10)—Si(4)—O(12)	109.1 (3)
O(3)—Si(2)—O(4)	105.2 (3)	O(11)—Si(4)—O(12)	109.7 (3)
O(3)—Si(2)—O(5)	112.0 (3)	O(12)—Si(5)—O(13)	110.9 (3)
O(3)—Si(2)—O(6)	104.5 (3)	O(12)—Si(5)—O(14)	109.9 (3)
O(4)—Si(2)—O(5)	117.4 (3)	O(12)—Si(5)—O(15)	104.6 (3)
O(4)—Si(2)—O(6)	112.9 (3)	O(13)—Si(5)—O(14)	113.3 (3)
O(5)—Si(2)—O(6)	104.2 (3)	O(13)—Si(5)—O(15)	110.2 (3)
O(6)—Si(3)—O(7)	110.7 (3)	O(14)—Si(5)—O(15)	107.8 (3)
O(6)—Si(3)—O(8)	107.9 (3)	Si(1)—O(3)—Si(2)	144.7 (4)
O(6)—Si(3)—O(9)	106.3 (3)	Si(2)—O(6)—Si(3)	140.7 (4)
O(7)—Si(3)—O(8)	116.7 (3)	Si(3)—O(9)—Si(4)	141.8 (4)
O(8)—Si(3)—O(9)	110.8 (3)	Si(4)—O(12)—Si(5)	132.1 (4)
		Si(5)—O(15)—Si(1)	134.1 (3)

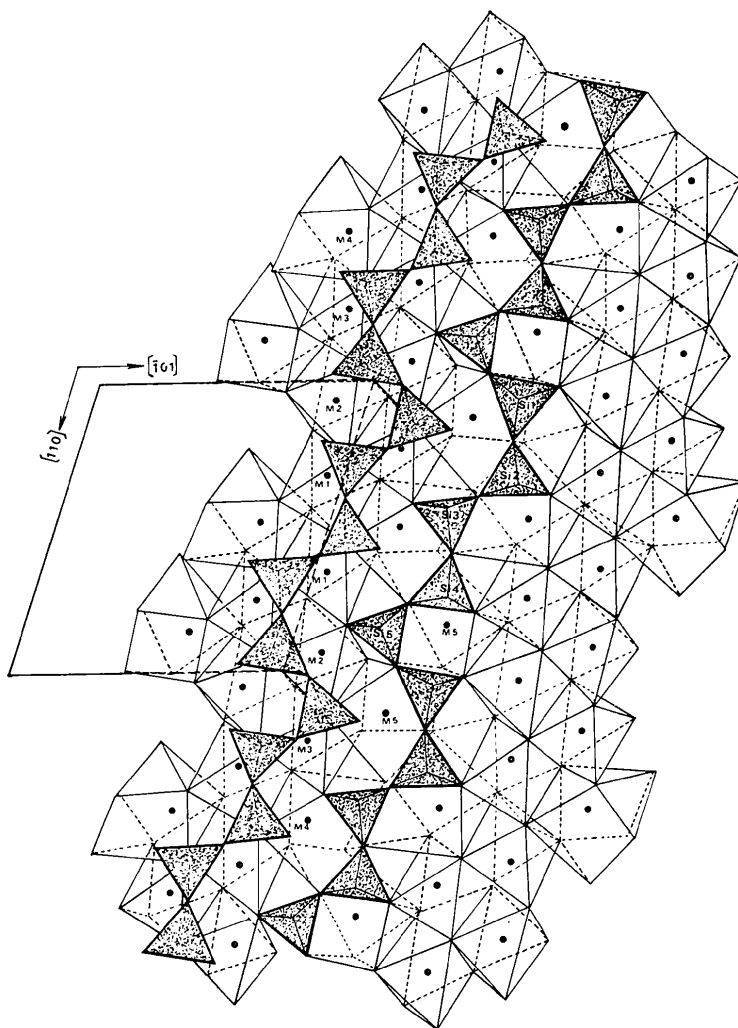


Fig. 2. A portion of the structure of nambulite projected on to $(1\bar{1}1)$. Metal-oxygen polyhedral bands are shown running parallel to $[110]$ in the layer. The left silicate chain has the apical oxygen pointing down; it runs between the bands and links the two metal-oxygen polyhedral bands in the next layer towards the viewer. The translated unit cell in the $(1\bar{1}1)$ plane is outlined on the left.

the closely packed sheet of oxygen atoms, in Fig. 2. The structure consists of infinite Mn polyhedral bands and infinite silicate chains with a repeat unit of five tetrahedra, parallel to [110]. The Mn polyhedral bands are composed of finite chains of eight polyhedra parallel to [341] by sharing edges with the adjacent chains.

Of five crystallographically different polyhedra, the M(1), M(2) and M(3) polyhedra are nearly regular octahedra. The mean values of the Mn–O distances are 2.233, 2.242 and 2.188 Å for the M(1), M(2) and M(3) polyhedra respectively.

The M(4) polyhedra at the ends of the polyhedral chains are irregular, with seven oxygen atoms, and are characterized by three long M–O bonds with a mean value of 2.752 Å and four short M–O bonds with a mean value of 2.145 Å. A similar feature of the bond distances at the ends of polyhedral chains is found in the synthetic rhodonite-type MnSiO₃ (Narita, 1973).

The Li and Na atoms occupy the M(5) site, which is the centre of a distorted square antiprism (Fig. 3). Two M(5) polyhedra share an edge and connect the bands of Mn polyhedra parallel to (1 $\bar{1}$ 1). A similar coordination of the Na atom is found in pectolite (Buerger, 1956; Buerger & Prewitt, 1961). The mean value, 2.369 Å, of the six M(5)–O distances is shorter than the 2.443 Å in the Na polyhedron in pectolite. This confirms random distribution of Li and Na atoms in the M(5) polyhedron, because Li⁺ is smaller than Na⁺. The random distribution of Li and Na atoms in nambulite suggests the possibility of a wide range of (Li,Na)Mn₄Si₅O₁₄(OH) solid solutions.

The most probable location of the hydrogen atom is between O(1) and O(11) (Fig. 3) within the silicate chains, which are linked to the Si(4) and Si(5) tetrahedra, respectively.

The distance of 2.464 (8) Å between O(1) and O(11) is shorter than those between the hydrogen-bonded oxygen atoms in pectolite and babingtonite, and is longer than the 2.453 (4) Å in serandite (Takéuchi & Kudoh, 1972). In spite of the difference in the number of cations, nambulite is more closely related to babingtonite than to rhodonite in the arrangement of silicate chains and polyhedral bands.

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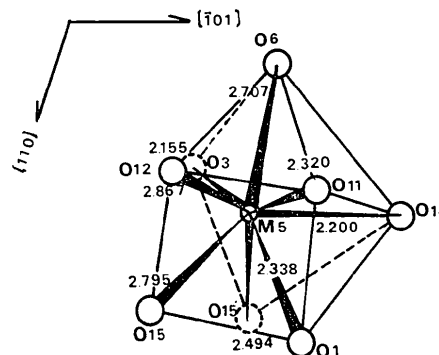


Fig. 3. The Li and Na atoms occupy the M(5) sites surrounded by eight oxygen atoms. This polyhedron is a distorted square antiprism.

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