

A refinement of the crystal structure of ohmilite, $\text{Sr}_3(\text{Ti}, \text{Fe}^{3+})(\text{O}, \text{OH})(\text{Si}_2\text{O}_6)_2 \cdot 2\text{--}3\text{H}_2\text{O}$

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Abstract

The monoclinic unit cell of ohmilite, $\text{Sr}_3(\text{Ti}, \text{Fe}^{3+})(\text{O}, \text{OH})(\text{Si}_2\text{O}_6)_2 \cdot 2\text{--}3\text{H}_2\text{O}$, has dimensions $a = 10.979(6)$, $b = 7.799(5)$, $c = 7.818(4)\text{\AA}$, $\beta = 100.90(3)^\circ$, and space group $P2_1/m$; $Z = 2$, $V = 657.4(6)\text{\AA}^3$. The crystal structure has been refined to an R -value of 5.9% for 2121 independent reflections. Vertex-sharing Ti–O octahedra form chains parallel to b . Each of the octahedral chains is flanked by a pair of $[\text{Si}_4\text{O}_{12}]$ chains, which are similar to those found in batisite and haradaite, thus forming a composite chain of composition $[\text{Si}_4\text{O}_{12}(\text{Ti}_2\text{O}_2)\text{Si}_4\text{O}_{12}]^{12-}$. These composite chains are joined together by Sr atoms and water molecules to form the structure. Of the three independent Sr atoms, Sr(1) and Sr(3) are 9-coordinated, with average Sr–O distances of 2.675\AA. Sr(2) is 8-coordinated, with average bond length of 2.586\AA. The average Ti(Fe)–O bond length is 1.992\AA. Average Si–O distances are 1.643 and 1.606\AA for bridging and nonbridging bonds, respectively. As consistent with the IR data, hydrogen is present as both H_2O and OH. The former forms hydrogen bonds with the oxygen atoms of the composite chains, with O–O distances from 2.69 to 2.83\AA. The latter is associated with the octahedral cations in accordance with the substitution scheme, $\text{Ti}^{4+}\text{O}^{2-} \rightarrow \text{Fe}^{3+}\text{OH}^-$.

Introduction

Ohmilite, $\text{Sr}_3(\text{Ti}, \text{Fe}^{3+})(\text{O}, \text{OH})(\text{Si}_2\text{O}_6)_2 \cdot 2\text{--}3\text{H}_2\text{O}$, was found in riebeckite–albite units in serpentinite from Ohmi, Niigata Prefecture, Central Japan and was described as a new mineral by Komatsu *et al.* (1973). It occurs as spherulites composed of radially arranged fine needles or fiber-like crystals which are generally less than 10 μm in diameter. The chemical analysis (Komatsu *et al.*, 1973) gave SiO_2 34.79, TiO_2 10.27, Fe_2O_3 0.20, SrO 47.37, H_2O_+ 6.68 with a total of 99.31 weight percent. The chemical formula $\text{Sr}_3\text{TiSi}_4\text{O}_{12}(\text{OH}) \cdot 2\text{H}_2\text{O}$ was proposed assuming that titanium is trivalent. However, according to a suggestion made by Dr. A. Kato the formula has been revised to $\text{Sr}_3\text{Ti}[\text{O}(\text{Si}_4\text{O}_{12})] \cdot 2\text{H}_2\text{O}$ or $\text{Sr}_3(\text{Ti}, \text{Fe}^{3+})[(\text{O}, \text{OH})\text{Si}_4\text{O}_{12}] \cdot 2\text{H}_2\text{O}$ such that the titanium is present as Ti^{4+} .

The crystal structure of ohmilite has been determined and refined to an R -value of 14% (Mizota *et al.*, 1973), showing that ohmilite has a chain structure similar to that of haradaite (Takéuchi and Joswig, 1967). The relatively

high value of the R -factor was due to the poor quality of the crystal used. Because we have recently found a crystal fragment of high quality, we have undertaken the refinement of the crystal structure. The present paper describes the detailed structure of ohmilite and discusses the configuration of the silicate chains and the role of the hydrogen atoms in conjunction with data from infrared absorption spectrometry and DSC-TG.

Experimental

X-ray diffraction

A crystal fragment having dimensions of approximately $0.6 \times 0.1 \times 0.04$ mm was used for the present study. Unit cell dimensions were determined utilizing a Philips PW1100 single-crystal diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71069\text{\AA}$). The cell dimensions, obtained by least-squares refinement with 25 independent reflections, are $a = 10.979(6)$, $b = 7.799(5)$, $c = 7.818(4)\text{\AA}$, $\beta = 100.90(3)^\circ$, $V = 657.4(6)\text{\AA}^3$.

The space group, $P2_1/m$, (Mizota *et al.*, 1973) has been confirmed with the extinction rule that $0k0$ reflections occur when k is even, and the results of the refinement. The ω - 2θ scan technique was used to measure intensities in one fourth of reciprocal space up to $2\theta = 70^\circ$ (MoK α monochromated radiation). Reflections were rejected whose intensities satisfied the relation $I_{\text{peak}} - 2\sqrt{I_{\text{peak}}} < I_{\text{back}}$. The 2121 reflections so obtained were corrected for Lorentz and polarization factors and for absorption ($\mu = 127.8 \text{ cm}^{-1}$), the latter being made using the ABCR program written by Mizota for the PW1100 System. Atomic scattering factors for cations were taken from the *International Tables for X-ray Crystallography, Vol. IV*; that for O^{2-} was provided by Tokonami (1965). Anomalous dispersion factors as obtained from the *International Tables for X-ray Crystallography, Vol. IV* were applied to all atoms.

Computations in this work were carried out using the UNICS II program system written by Sakurai *et al.* (1974) and applied to the FACOM M-200 system of the Computer Center of Kyushu University by Kawano (1980). Some corrections of reflection data were done at the Computer Center of Yamaguchi University.

Structure refinement

Initial atomic parameters were taken from the work of Mizota *et al.* (1973). Least-squares refinement with isotropic temperature factors converged to $R = 9.8\%$. Unit weight was applied for the least-squares refinement throughout this work. Several cycles with anisotropic temperature factors caused the R -value to decrease to 6.1%. Electron density and difference electron density

maps at this stage showed a peak at (0.5,0.25,0.0) in a cavity of the structure, suggesting the existence of an additional oxygen atom of a water molecule. As the temperature factor of this atom, designated W(3), diverged in successive cycles of refinement, its site occupancy was refined. The occupancy converged to 0.274(9) which corresponds to the multiplicity factor of 0.137 as given in Table 1. Occupancies of other oxygen atoms showed no significant change from values corresponding to full occupancy. This implies that the occupancy factor determined for W(3) is accurate. After several cycles of least-squares refinement which included W(3), the R -factor decreased to 5.9% with unit weight for all structure factors. The final set of F_o and F_c values is given in Table 2.¹

The final atomic parameters are listed in Table 1. The designations of some oxygen atoms are changed from those of Mizota *et al.* (1973). The positions of the hydrogen atoms of water molecules could not be determined.

Description of the structure and discussion

Outline of the structure

The b -axis projection of the structure is illustrated in Figure 1. The TiO_6 octahedra are joined by sharing vertex

¹ To receive a copy of Table 2, order Document AM-83-222 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N. W., Washington, D. C. 20009. Please remit \$1.00 in advance for the microfiche.

Table 1. Atomic coordinates and anisotropic temperature factors for ohmilite

Atom	M	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sr(1)	0.5	0.1107(1)	1/4	0.3523(1)	19(1)	24(1)	26(1)	0	7(1)	0
Sr(2)	0.5	0.4164(1)	1/4	0.7175(1)	15(1)	21(1)	42(1)	0	10(1)	0
Sr(3)	0.5	0.2667(1)	3/4	0.3916(1)	19(1)	18(1)	29(1)	0	10(1)	0
Ti	0.5	0	0	0	14(1)	176(5)	19(2)	14(2)	4(1)	-17(3)
Si(1)	1.0	0.2989(2)	0.4532(3)	0.1160(2)	15(1)	15(2)	24(2)	0(1)	4(1)	-1(2)
Si(2)	1.0	0.2054(2)	0.5470(2)	0.7418(2)	18(1)	11(2)	24(2)	0(1)	10(1)	0(2)
O(1)	0.5	0.0278(8)	1/4	0.0033(10)	23(7)	32(10)	41(10)	0	13(7)	0(2)
O(2)	1.0	0.1669(5)	0.5289(7)	0.1486(6)	18(4)	23(7)	34(7)	0(4)	3(4)	-8(5)
O(3)	1.0	0.0665(5)	0.5267(7)	0.7762(6)	20(4)	24(7)	31(6)	-2(4)	10(4)	1(5)
O(4)	0.5	0.2972(8)	1/4	0.1691(10)	31(7)	13(9)	32(10)	0	9(6)	0
O(5)	0.5	0.2417(8)	3/4	0.7344(10)	38(7)	5(9)	47(11)	0	25(7)	0
O(6)	1.0	0.4108(5)	0.5446(7)	0.2410(7)	25(4)	26(7)	43(7)	-5(4)	2(4)	-11(6)
O(7)	1.0	0.2337(5)	0.4572(7)	0.5698(6)	30(4)	15(6)	33(7)	1(4)	11(4)	-8(5)
O(8)	1.0	0.3039(5)	0.4610(7)	0.9070(6)	20(4)	29(7)	33(7)	6(4)	12(4)	7(6)
W(1)	0.5	0.0283(7)	3/4	0.4096(10)	17(6)	37(11)	41(11)	0	-1(6)	0
W(2)	0.5	0.5077(8)	1/4	0.4323(11)	30(7)	54(12)	46(11)	0	6(7)	0
W(3)	0.137	0.521(6)	1/4	0.029(15)	110(70)	50(80)	1300(400)	0	330(150)	0

M: Multiplicity factor. W: Oxygen atom of a water molecule.

Anisotropic temperature factors in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + \beta_{23}kl)]$, multiplied by 10^4 . Estimated standard deviations are given in parentheses.

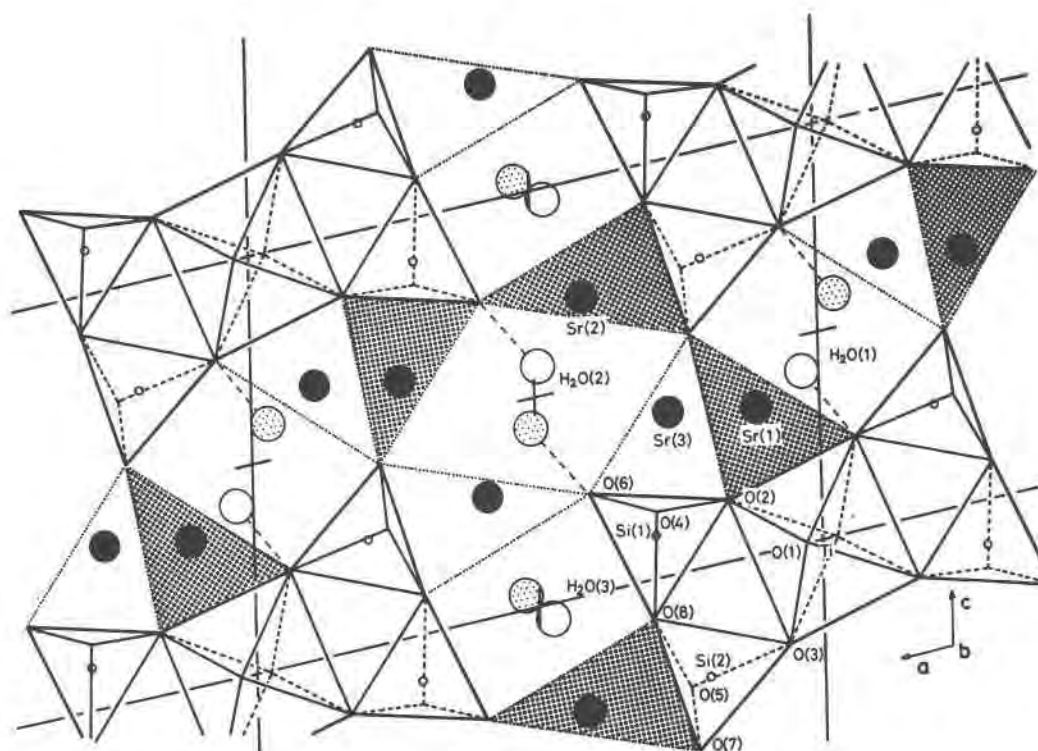


Fig. 1. Diagram of the ohmilite structure projected parallel to *b*. Sr atoms (large solid circles) in dotted triangles are in mirror planes at $y = 1/4$ and those in blank triangles are at $y = 3/4$. Open large circles and dotted ones depict oxygens of water molecules and lie in mirror planes at $y = 3/4$ and $1/4$, respectively. Doubly dashed lines indicate the two directions of hydrogen bonds corresponding to a water molecule.

oxygen atoms to form a chain parallel to *b*, the shared oxygen atoms being in the mirror planes perpendicular to the chain extension. A salient feature of the structure is that each octahedral chain thus formed is flanked by a pair of silicate chains, each having chemical composition $[\text{Si}_4\text{O}_{12}]$ (Fig. 2). The resulting composite chain has the shape of a rod and has the composition $(\text{Si}_4\text{O}_{12}(\text{Ti}_2\text{O}_2)\text{Si}_4\text{O}_{12})^{12-}$. Three symmetrically-independent Sr^{2+} ions and three water molecules are located in the mirror planes and both play rolls in joining together the above-mentioned rods to form the composite crystal structure. Interatomic distances and angles are given in Table 3.

Sr-polyhedra

Each Sr ion is located approximately at the center of a distorted trigonal prism formed by oxygen atoms associated with the rods. The Sr ions are also coordinated by two or three additional oxygen atoms of water molecules as shown in Figures 1 and 3. Sr(1) and Sr(3) thus have nine-fold coordination (both with average bond lengths 2.674\AA) while Sr(2) has eight-fold coordination (average bond length 2.454\AA). Even if we do not take the short Sr(2)–W(3) distance into account because of the partial occupation of W(3), the average Sr–O bond length of the Sr(2)-polyhedron is 2.599\AA and is the shortest of the three

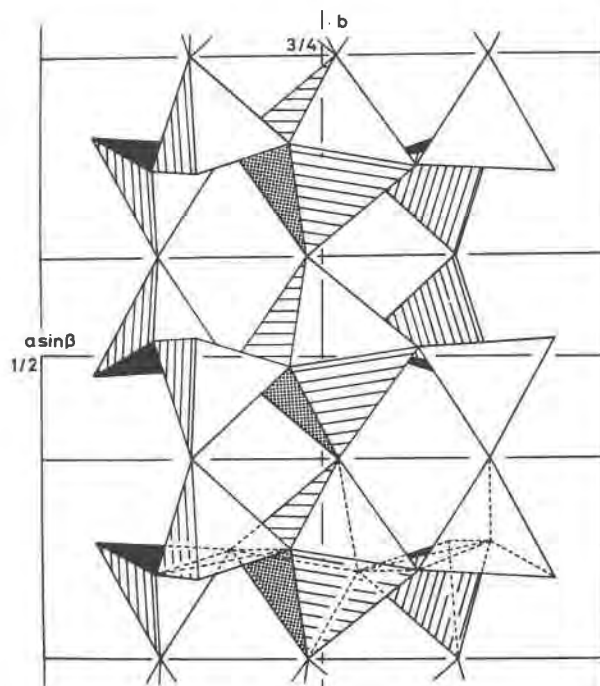


Fig. 2. The rod structure of $[\text{Si}_4\text{O}_{12}(\text{Ti}_2\text{O}_2)\text{Si}_4\text{O}_{12}]^{12-}$ as composed of a Ti-octahedral chain and a pair of Si–O single chains.

Table 3. Interatomic distances and bond angles

Sr polyhedra					
Sr(1)-O(2) ×2	2.828(5) Å	Sr(2)-O(6) ×2	2.454(5) Å	Sr(3)-O(2) ×2	2.642(4) Å
-O(3) ×2	2.654(5)	-O(7) ×2	2.660(7)	-O(6) ×2	2.675(5)
-O(7) ×2	2.535(4)	-O(8) ×2	2.664(7)	-O(7) ×2	2.727(5)
-O(4)	2.714(8)	-W(2) I	2.605(10)	-O(5)	2.742(7)
-O(1)	2.709(7)	-W(3)	2.524(10)	-W(1)	2.645(7)
-W(1)	2.614(7)	Average-----	2.585	-W(2) I	2.596(8)
Average-----	2.674	---[omit. W(3)	2.594]	Average-----	2.674
Ti octahedron					
Ti-O(1)*	1.969(1) Å	O(1)-O(2)	2.767(6) Å	O(1)-Ti-O(2)	88.8(2)°
-O(2)	1.986(4)	O(1)I-O(2)	2.825(7)	-O(3)	88.1(3)
-O(3)	2.021(5)	O(2)-O(3)	2.910(6)	O(2)-Ti-O(3)	86.9(2)
Average-----	1.992	-O(3)I	2.755(8)	O(3)-O(2)-O(3)I	91.0(2)
		O(1)-O(3)	2.867(7)	-O(1)-O(3)I	91.5(2)
		-O(3)I	2.775(8)	O(1)-O(2)-O(1)I	89.5(2)
		Average-----	2.816	Ti-O(1)-Ti b	162.4(4)
Si tetrahedra					
Si(1)-O(2)	1.628(5) Å	Si(2)-O(3)	1.616(5) Å	Si(1)-O(4)-Si(1)m b	150.3(5)°
-O(4)*	1.636(2)	-O(5)*	1.632(3)	Si(2)-O(5)-Si(2)m b	151.0(6)
-O(6)	1.585(5)	-O(7)	1.595(5)	Si(1)-O(8)-Si(2) b	130.3(3)
-O(8)*	1.643(5)	-O(8)*	1.661(5)		
Average-----	1.623	Average-----	1.626	Average bridge Si-O	-----1.643 Å
O(8)-Si(1)-O(2)	109.9(2)°	O(8)-Si(2)-O(3)	109.3(3)°	Average non-bridge Si-O	-----1.606 Å
-O(6)	115.2(3)	-O(7)	105.9(3)		
-O(4)	106.9(3)	-O(4)	107.0(3)		
O(4)-Si(1)-O(2)	104.8(3)	O(5)-Si(2)-O(3)	110.2(3)		
-O(6)	108.8(3)	-O(7)	107.8(3)		
O(2)-Si(1)-O(6)	110.7(3)	O(3)-Si(2)-O(7)	116.2(3)		
Related to H ₂ O					
W(1)-O(3)I ×2	2.688(6) Å	W(2)I-O(6) ×2	2.831(6) Å	W(3)-O(4)	2.83(8) Å
O(3)-W(1)-O(3)m	106.3(3)°	-O(4)	2.785(10)	-O(5)	2.90(9)
		O(6)-W(2)I-O(6)m	108.1(3)°	-O(6) 2	2.90(9)
				-O(8) 2	2.95(9)
				O(4)-W(3)-O(5)I	122(4)°
				O(8)-W(3)-O(8)m	99(2)
				O(6)-W(3)-O(8)m	105(3)
				-O(6)m	93(3)

* Bridging oxygen of Ti-O or Si-O chains.

W: Oxygen atom of each water molecule.

Atoms indicated with letters "I" or "m" are those produced by the inversion or the mirror operations (Fig. 1).

"b" shows the bridging M-O-M angle of the chain structure.

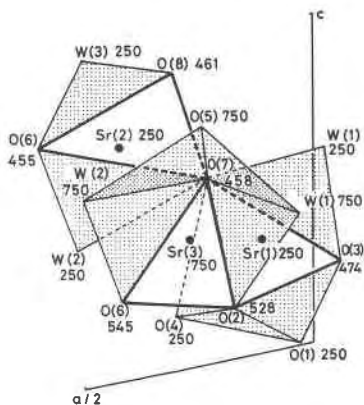


Fig. 3. Sr-O polyhedra projected onto (010). Triangles outlined by heavy lines show terminal faces of deformed trigonal prisms. The y-coordinate ($\times 1000$) for each atom is shown with three digits.

Sr-polyhedra (Table 3). Sr(1)- and Sr(3)-polyhedra join Ti-Si-rods along c, whereas Sr(2)-polyhedra join them along a (Fig. 1).

Ti-octahedron

The bridging Ti-O bond length is shorter than the non-bridging values. The average value of Ti-O bond lengths, 1.992 Å, is very close to the bond lengths for $^{VI}Ti^{4+}-^{IV}O^{2-}$ or $^{VI}Ti-^{V}O^{2-}$, 1.98-1.99 Å, given by Shannon and Prewitt (1968). This supports the conclusion that the valence state of Ti is Ti^{4+} .

One of the anisotropic temperature factor coefficients of the Ti-atom, β_{22} , is abnormally large (Table 1). As shown in Figure 4, the electron density of this atom clearly shows an elongation along b. This suggests a statistical displacement of Ti^{4+} from the center of the octahedra. It is, however, not possible to decide whether

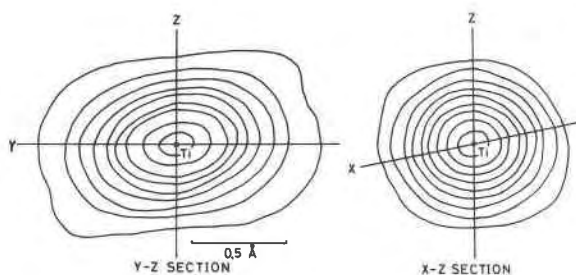


Fig. 4. Electron density around the Ti atom. Y - Z and X - Z sections at $(0,0,0)$ are shown. Contour line interval: $20 \text{ e}/\text{\AA}^3$. Lines at zero-density are not shown.

the displacement is due to positional disorder or thermal vibration.

The configuration of the silicate chain

The average length of the bridging bonds (1.643\AA) is longer than that of the non-bridging bonds (1.606\AA). These values are very close to 1.641 and 1.605\AA given as averages for non-linear chains by Takéuchi and Joswig (1967).

The configuration of the silicate chains is in accord with the infrared spectrum of ohmilite (Fig. 5) which we obtained with a Nihon-bunko IRA-2 spectrometer using the KBr disk method of specimen preparation. The spectra gave four absorption bands at 575 , 636 , 678 and 746 cm^{-1} . Absorption bands in the range 530 – 775 cm^{-1} have been assigned by Ryall and Threadgold (1966) to correspond to the Si–O–Si symmetrical stretching of single chains of pyroxenes and pyroxenoids. They have pointed out that the number of bands in this region corresponds to the number of tetrahedra in the repeat unit of the single silicate chain. The structurally related mineral batisite also has four tetrahedra in the repeat unit and has four bands at 573 , 634 , 713 and 768 cm^{-1} (Lazarev, 1968). The absorption bands of both minerals are similar in frequency.

Similar Si_4O_{12} chains occur as parts of the structures of ohmilite, batisite, haradaite and $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$, and the configurations of these chains are shown in Figure 6. The manner in which the full crystal structures are constructed with the silicate chains is also different, as follows: (1) In batisite, the Si_4O_{12} chains and the Ti-octahedral chains share apical oxygens to form a three-dimensional structure (Nikitin and Belov, 1962); (2) Haradaite and $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$ (Kawamura and Kawahara, 1976) are "quasi-layer silicates" as defined by Takéuchi and Joswig (1967), in which Si–O chains are joined together by V- and Cu-polyhedra, respectively, to make sheet structures extending infinitely in two dimensions; and (3) Ohmilite forms the rod structure described above (Fig. 2). The Si_4O_{12} and the Ti-octahedral chains constitute a one-dimensionally elongated structure.

H_2O and the hydrogen bonding

Considering interatomic distances and angles related to the oxygen atoms of water molecules and neighboring oxygens (Table 3), we find that W(1) and O(3) should be hydrogen bonded. The W(1)–O(3) distance (2.688\AA) and O(3)–W(1)–O(3)_m angle (106.3°) are reasonable values for hydrogen bonding, where the letter "m" indicates the mirror operation.

W(2) is hydrogen-bonded to O(6) (Fig. 1), as implied by the W(2)–O(6) distance which has a relatively small value of 2.831\AA ; the O(6)–W(2)–O(6)_m angle is 108.1° . W(2) has a short bond length to O(4) of 2.785\AA . Since, however, O(4) is a bridging oxygen in the silicate chain, the formation of a hydrogen bond between W(2) and O(4) is less likely; the Si–O(4) bond distance is not unusual (2.714\AA). The neighbors of W(3) are at distances greater than 2.9\AA , excluding the distance of 2.83\AA between W(3) and the bridging oxygen, O(4). This suggests that the structure may be stable without W(3). This may account for the deficiency of water at the W(3) site.

IR-spectra and DSC-TG for H_2O

Ohmilite gives a small but sharp IR-peak at 1394 cm^{-1} . An absorption band similar to this has been found in pectolite at 1395 cm^{-1} and is explained by Ryall and Threadgold (1966) as due to an OH bending mode. There is no direct proof of the presence of an OH group in ohmilite from the viewpoints of structure and chemistry. However, if Fe^{3+} replaces Ti^{4+} , this should be coupled with OH^- substitution for O^{2-} to maintain charge valence. The ohmilite analysis does give $0.2\% \text{ Fe}_2\text{O}_3$. Broad peaks at 1571 and 1725 cm^{-1} are considered to be due to the OH stretching vibration of a very strong hydrogen bond (Nakamoto *et al.*, 1955).

Nakamoto *et al.* (1955) have demonstrated a linear relationship between the OH–O bond distance and wavenumber. Considering this relation, the strong, broad peak around 3000 cm^{-1} for ohmilite is attributed to an OH–O bond with a length of 2.7 – 2.9\AA which is the same range of lengths for the hydrogen bond related to water molecules as determined by X-ray refinement. The small but relatively sharp peak at 1610 cm^{-1} is assigned to adsorbed water. The DSC-TG curves obtained with a

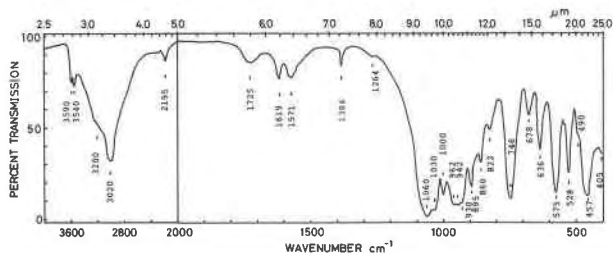


Fig. 5. Infrared absorption spectra of ohmilite. Wavenumber (cm^{-1}) of each peak is given.

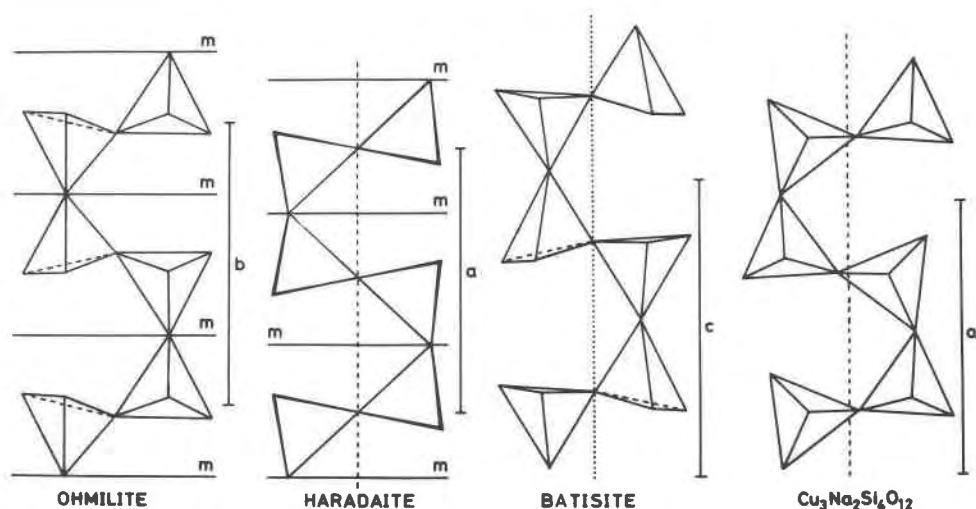


Fig. 6. Batisite-type Si_4O_{12} chains found in ohmilite, haradaite (Takéuchi and Joswig, 1967), batisite (Nikitin and Belov, 1962) and Cu-Na-silicate (Kawamura and Kawahara, 1976). Broken lines and a dotted line indicate a -glide planes and c -glide planes, respectively. Solid lines with the letter "m" are mirror planes. Unit cell edges along the chain length are shown.

Rigaku DSC-TG (8085E1) indicates that the dehydration occurs over a wide temperature range in several steps between 250° and 600°C. The DSC curve we obtained did not permit further analysis because of its poor quality, this being possibly due to the very small amount of sample (6.5 mg) and contamination by organic material which produced the unusual exothermic peak at approximately 300°C.

On the chemical formula of ohmilite

The chemical formula of ohmilite may now be expressed by $\text{Sr}_3(\text{Ti}, \text{Fe}^{3+})(\text{O}, \text{OH})(\text{Si}_2\text{O}_6)_2 \cdot 2-3\text{H}_2\text{O}$, $Z = 2$. The partial replacement of $\text{Ti}^{4+}\text{O}^{2-}$ by $\text{Fe}^{3+}\text{OH}^-$ is apparent from the chemical constituents and the presence of the OH absorption band in the infrared spectrum. The chemical composition of the silicate chains in ohmilite, batisite and related minerals should be expressed as $(\text{Si}_2\text{O}_6)_2$ rather than Si_4O_{12} because they have two symmetrically independent tetrahedra in the repeat unit. The variable occupancy of W(3) is responsible for the following relations: With the occupancy of W(3) deduced from the structure refinement and neglecting the small amount of Fe, the formula is $\text{Sr}_3\text{TiO}(\text{Si}_2\text{O}_6)_2 \cdot 2.27 \text{H}_2\text{O}$. The water content for this formula is 6.23% and is comparable with 6.68% as obtained by ignition. The TG data showed a higher water content in the range 9.0–9.6%, but this is less reliable because of the very small amount of sample used and the contamination mentioned above. If W(3) is fully occupied the water content is 8.08%. Further work is necessary on the water problem but it is now impossible as not enough material is available.

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