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# The crystal structure of synthetic $\mathrm{Mg}^{\mathrm{IV}}$ mica

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## Auszug

Die Kristallstruktur eines aus Talk und Kaliumcarbonat unter hydrothermalen Bedingungen synthetisch dargestellten Glimmers wurde bestimmt und bis zu $R = 0{,}092$ verfeinert. Der Glimmer ist Mg-reich und frei von Al; das Mg befindet sich in Si-Lagen, die außerdem zum Teil unbesetzt sind. Er stellt ein Übergangsglied zwischen di- und trioktaedrischem Typ dar. Die Gitterkonstanten sind $a = 5{,}321(2)$, $b = 9{,}238(1)$, $c = 10{,}287(1)$ Å, $\beta = 100{,}06(1)°$; Raumgruppe $C2/m$, $Z = 1$. Aus der Verfeinerung ergab sich als chemische Formel

$$\mathrm{K_2(Mg_{5,60}\square_{0,40})(Si_{7,32}Mg_{0,68})O_{20}(OH)_4}.$$

Aus dem mittleren Abstand (Si,Mg)—O $= 1{,}649 \pm 0{,}006$ Å kann geschlossen werden, daß Mg 8,5% der tetraedrischen Lagen besetzt; aus der chemischen Formel ergeben sich für Mg 7,6%. Die (O—O)-Abstände parallel zur Basis unterscheiden sich nur wenig von den Abständen zum O-Atom in der Tetraederspitze; die letzteren sind um etwa 0,018 Å größer als die in der Basis. Auch die Abstände der K-Ionen zu den nächsten O-Ionen in den beiden dem Kalium benachbarten Tetraederschichten sind nicht sehr verschieden; die beiden Mittelwerte sind 3,010 Å und 3,346 Å. Der beobachtete Drehungswinkel der Tetraeder ist 7,10°, in guter Übereinstimmung mit dem früher berechneten Wert.

## Abstract

The crystal structure of a mica, which was synthesized from talc and potassium carbonate under a hydrothermal condition, was determined by least-squares methods. The mica is a Mg-rich free from Al ions, with Mg ions substituting for Si, and with some vacant positions in the octahedral sites. This mica is intermediate between the trioctahedral and dioctahedral types and agrees with a Mg-rich mica first reported by Seifert and Schreyer (1971). The lattice parameters are: $a = 5.321(2)$, $b = 9.238(1)$, $c = 10.287(1)$ Å and $\beta = 100.06°(1)$. The space group is $C2/m$ with $Z = 1$. The final residual is $R = 9.2\%$ using anisotropic temperature factors. The refinement gave the structural formula:

$$\mathrm{K_{2.00}(Mg_{5.60}\square_{0.40})(Si_{7.32}Mg_{0.68})O_{20}(OH)_4},$$

where □ means a vacant position. In the light of this result, the structural formula may be shown from the chemical composition as:

$$(K_{1.92}Na_{0.07})(Mg_{5.68}\square_{0.32})(Si_{7.26}Mg_{0.61}Fe_{0.07}Al_{0.06})O_{20}(OH)_4,$$

where small amounts of Al and Fe ions are included in the tetrahedral sites. (Si,Mg)—O distance, 1.649 ± 0.006 Å in average, suggests 8.5% substitution of Mg ions in the tetrahedral sites, which is close to 7.6% in the above formula. The difference between the mean basal O—O distance and the mean basal-apical O—O distance is small (0.018 Å). Inner and outer K—O distances are 3.010 Å and 3.346 Å in average respectively. The observed tetrahedral rotation angle (7.10°) is close to the value calculated by the equations previously reported.

## Introduction

Trioctahedral and dioctahedral micas show a wide range of isomorphous substitution of ions. Hazen and Wones (1972) showed the upper limit of the ionic radius of the cation substituting the octahedral sites is 0.78 Å in average, whereas the radius of the cation substituting the tetrahedral site ranges from the order of the radius of boron (0.12 Å) to that of trivalent iron (0.49 Å). Valencies of cations substituting the tetrahedral site range also from $2^+$ to $4^+$ as $Fe^{3+}$ in annite and iron phlogopite (Donnay *et al.*, 1964; Steinfinc, 1962) and $Mn^{2+}$ in manganese mica (Daimon *et al.*, 1961). Recently Seifert and Schreyer (1971), for the first time, studied on synthetic magnesium micas with magnesium ions located in the tetrahedral sites.

In the course of the study on artificial alteration of talc and tremolite, we found the formation of a Mg mica free Al ions. The mica has Mg ions substituting for Si in the tetrahedral sites, and some vacant octahedral sites and is an intermediate between the trioctahedral and dioctahedral types. The property of the mica agrees with that of a magnesium-rich mica, $K_2Mg_{5.75}(Si_{7.25}Mg_{0.75})O_{20}(OH)_4$, reported by Seifert and Schreyer (1971). For the sake of convenience, the present mica will be called as $Mg^{IV}$ mica.

Existence of vacancy in the octahedral sites of the present mica was also proved by the infrared absorption spectra and TG analyses, the result will be published elsewhere.

## Experimental

Powder of talc of 100—150 mesh in size was used for a starting mineral. Its chemical composition is shown in Table 1. A mixture of talc, potassium carbonate and water in the ratio as 1:10:10 was sealed in a silver tube and treated under a hydrothermal condition of temperature, 500 °C, and pressure, 500 atm, during 15 days. The original talc has completely altered to the $Mg^{IV}$ mica.

Table 1. *Chemical compositions and structural formulas calculated on the basis 22 $O^{2-}$ of talc and synthesized mica*

| | I | | | II | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | (1) | | | (2) | |
| $SiO_2$ | 61.72% | 7.99 | 8.00 | 51.93% | 7.26 | 8.00 | 7.26 | 7.39 |
| $Al_2O_3$ | 0.28 | 0.01 | | 0.36 | 0.06 | | 0.06 | |
| | | 0.03 | 5.86 | | | | | |
| $Fe_2O_3$ + FeO | 0.54 | 0.05 | | 0.65 | 0.07 | | 0.07 | |
| MgO | 29.98 | 5.78 | | 30.19 | 0.61 | | 6.29 | 6.29 |
| | | | | | 5.68 | 5.68 | | |
| $Na_2O$ | 0.85 | 0.21 | 0.21 | 0.28 | 0.07 | 1.99 | 0.07 | 1.99 |
| $K_2O$ | 0.01 | | | 10.77 | 1.92 | | 1.92 | |
| $H_2O$ (−) | 0.98 | | | 0.39 | | | | |
| $H_2O$ (+) | 4.96 | | | 4.91 | | | | |
| Total | 99.32 | | | 99.48 | | | | |

I. Talc used as the starting material, Kaijo, Korea.
II. Mica used in this structure determination.

## Lattice parameters

Lattice parameters were determined from x-ray powder data (Table 2). *b* Parameter of this mica is larger than that of the usual

Table 2. *Cell dimensions and chemical formulas of trioctahedral micas*

| | *a* | *b* | *c* | *β* |
|---|---|---|---|---|
| (1) Synthetic fluorophlogopite McCAULEY, NEWNHAM and GIBBS (1973) | 5.308(2) Å | 9.183(3) Å | 10.139(1) Å | 100.07(2)° |
| (2) Mg-rich mica SEIFERT and SCHREYER (1971) | 5.329(5) | 9.246(8) | 10.277(10) | 100.02(6) |
| (3) Si-rich mica SEIFERT and SCHREYER (1971) | 5.256(5) | 9.089(8) | 10.201(10) | 99.98(9) |
| (4) Present mica | 5.321(2) | 9.238(1) | 10.287(1) | 100.06(1) |

(1) $(K_{1.96}Na_{0.08})(Mg_{5.94})(Al_{2.04}Si_{5.96})O_{19.80}F_{3.88}(OH)_{0.32}$
(2) $K_2(Mg_{5.75}\square_{0.25})(Si_{7.25}Mg_{0.75})O_{20}(OH)_4$
(3) $K_2(Mg_{5.0}\square_{1.0})Si_{8.0}O_{20}(OH)_4$
(4) $(K_{1.92}Na_{0.07})(Mg_{5.68}\square_{0.32})(Si_{7.26}Mg_{0.61}Fe_{0.07}Al_{0.06})O_{20}(OH)_4$

phlogopite and is close to Mg rich mica, $K_2Mg_{5.75}(Si_{7.25}Mg_{0.75})O_{20}(OH)_4$, reported by SEIFERT and SCHREYER (1971). The larger parameter is due to the substituting Mg ions in the tetrahedral sites.

## Structure determination

Diffraction spots distributing along $c^*$ direction are usually diffuse in the starting mineral, talc, whereas they are sharp in the synthesized mica. This fact shows that piling of layers becomes more order in the mica than talc because of fixation of potassium ions in the interlayer region.

Two crystal flakes were used for structure analysis, one is a lath-shaped crystal elongated to *a* axis and the other shows a platy crystal. The lath-shaped crystal ($0.4 \times 0.15 \times 0.10$ mm) shows extremely weak extra spots and diffuse streaks on long-exposure Weissenberg photographs.

Intensities of reflections, 385 in total, were measured on Weissenberg photographs of four levels (zero, first, second and third levels) about *a*-axis rotation, and of zero level about *b*-axis rotation using multiple-film technique and microphotometer and filtered Cu$K\alpha$ radiation. Intensities of just visible reflections were assigned to be one half of the minimum intensity of the reflections. Fe$K\alpha$ radiation is used to measure the intensities of some $hkl$ reflections ($l = 0, -1$ and 1) in order to obtain a good resolution between two neighbouring spots.

Platy crystal ($0.3 \times 0.4 \times 0.05$ mm) shows weak Debye-Scherrer arcs on the rotation photograph, which could not be cut away by layer-line screen. Therefore this crystal was only used for the intensity measurement of $0kl$ reflections.

The space groups $C2$, $Cm$ and $C2/m$ are considered in the solution of the structure. In the case of $C2$ and $Cm$, the refinement could not proceed because some atoms gave negative isotropic temperature factors. But the examination of the ROGERS and WILSON's test (1953) suggested the presence of a center of symmetry. On these evidences the space group $C2/m$ is proposed for the present mica.

The intensities were corrected for Lorentz, polarization and absorption factors.

## Refinement of structure

In the first step, an electron-density projection map was made using the atomic coordinates of the synthetic lithium fluormica (TAKEDA and DONNAY, 1966), atomic scaterring factors of $K^+$, $Mg^{2+}$

and $Si^{4+}$ (*International tables for x-ray crystallography*) and the value of $O^{2-}$ (Tokonami, 1965).

The structural formulas on the basis of $O_{20}(OH)_4$ are assigned in two ways with regard to the location of Mg ions: one shows $(Si,Mg)_8$ and some vacant octahedral sites as

$$(K_{1.92}Na_{0.07})Mg_{5.68}(Si_{7.26}Mg_{0.61}Fe_{0.07}Al_{0.06})O_{20}(OH)_4 \ , \qquad (1)$$

the other shows the octahedral composition $(Mg)_{6.29}$ and some tetrahedral vacant sites as

$$(K_{1.92}Na_{0.07})Mg_{6.29}(Si_{7.26}Fe_{0.07}Al_{0.06})O_{20}(OH)_4 \ . \qquad (2)$$

In order to approach to the most probable structural formula, the full-matrix least-squares refinement of the crystal-structure analysis was carried with the aid of the program (Busing, Martin and Levy, 1962) adapted by T. Sakurai for the HITTAC 5020 E.

Table 3. *Final atomic coordinates and equivalent isotropic temperature factors for synthetic* $Mg^{IV}$ *mica*

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$ |
|---|---|---|---|---|
| K | 0 | 0.5 | 0 | 3.82(15) Å² |
| O(1) | 0.019(3) | 0 | 0.1686(11) | 2.91(3) |
| O(2) | 0.3294(17) | 0.2320(9) | 0.1720(7) | 2.92(18) |
| Si, Mg | 0.0759(6) | 0.1665(3) | 0.2293(2) | 1.50(8) |
| O(3) | 0.1287(12) | 0.1668(6) | 0.3889(6) | 1.43(14) |
| OH | 0.636(2) | 0 | 0.3956(9) | 1.57(19) |
| Mg(1) | 0 | 0 | 0.5 | 1.1(2) |
| Mg(2) | 0 | 0.3325(5) | 0.5 | 1.04(14) |

The result of the refinement based upon the above substitution type (1) ($R = 10.4\%$) is reasonable (Table 3), because the result of the refinement based upon the substitution type (2) ($R = 10.8\%$) shows unusual temperature factors of Mg(1) and Mg(2) in the octahedral sites which are larger than that of silicon (Table 4). The final residual is $R = 9.2\%$ with anisotropic temperature factor (Table 5). As a result of these refinements, the site occupancy of the octahedral sites is $(Mg_{1.93}\square_{0.07})$ for position Mg(1) and $(Mg_{3.67}\square_{0.33})$ for position Mg(2). The final structural formula is given by

$$K_{2.00}(Mg_{1.93}\square_{0.07})\ (Mg_{3.67}\square_{0.33})\ (Si_{7.32}Mg_{0.68})O_{20}(OH)_4 \ .$$

Table 4. *Atomic coordinates and isotropic temperature factors obtained with chemical formula* (2)

| Atom | $x/a$ | $y/b$ | $z/c$ | $B$ |
|---|---|---|---|---|
| K | 0 | 0.5 | 0 | 3.27(17) Å$^2$ |
| O(1) | 0.021(3) | 0 | 0.1699(13) | 2.7(3) |
| O(2) | 0.329(2) | 0.2315(11) | 0.1716(9) | 2.7(2) |
| Si, □ | 0.0762(8) | 0.1665(4) | 0.2292(3) | 1.30(9) |
| O(3) | 0.1290(18) | 0.1668(8) | 0.3888(7) | 1.52(16) |
| OH | 0.637(3) | 0 | 0.3962(11) | 1.81(15) |
| Mg(1) | 0 | 0 | 0.5 | 1.34(15) |
| Mg(2) | 0 | 0.3327(6) | 0.5 | 1.47(11) |

Table 5. *Anisotropic thermal parameters in* Mg$^{\mathrm{IV}}$ *mica*

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| K | 0.037(4) | 0.0097(8) | 0.0065(6) | 0 | 0.0030(11) | |
| O(1) | 0.0225(11) | 0.007(7) | 0.0091(13) | 0 | 0.002(2) | |
| O(2) | 0.029(5) | 0.0099(11) | 0.0064(8) | −0.0054(18) | 0.0016(14) | −0.0007(8) |
| Si, Mg | 0.010(2) | 0.0037(3) | 0.0048(3) | −0.0005(5) | 0.0007(4) | −0.0001(2) |
| O(3) | 0.001(3) | 0.0037(7) | 0.0059(7) | −0.0007(13) | 0.001(10) | 0.0001(5) |
| OH | 0.017(7) | 0.0043(11) | 0.0041(9) | 0 | 0.0005(11) | |
| Mg(1) | 0.004(4) | 0.0032(7) | 0.0041(6) | 0 | 0.0005(10) | |
| Mg(2) | 0.005(3) | 0.0027(5) | 0.0030(4) | 0 | 0.0014(7) | |

Referring to the result of the above refinement, we can made the structural formula from the chemical composition as follows:

$$(\mathrm{K}_{1.92}\mathrm{Na}_{0.07})\ (\mathrm{Mg}_{5.68}\square_{0.32})\ (\mathrm{Si}_{7.26}\mathrm{Mg}_{0.61}\mathrm{Fe}_{0.07}\mathrm{Al}_{0.06})\mathrm{O}_{20}(\mathrm{OH})_4\ .$$

It is difficult to determine the positions of small amounts of Al and F$^{\mathrm{e}}$ ions. The above formula was made so as to fill the total number of the tetrahedral cations by Fe and Al along with Si and Mg ions.

Potassium ions have the largest thermal vibration amplitude among ions in Mg$^{\mathrm{IV}}$ mica. Basal oxygen atoms, O(1) and O(2), which are weakly bounded to the potassium ions but strongly surrounded by the tetrahedral cations, have higher temperature factors than O(3) which is surrounded by three Mg ions and one tetrahedral cation. This fact supports the concept of BURNHAM (1965) that the magnitude of the isotropic temperature factor of oxygen is intimately related to the number of coordination. The calculated value of the density is obtained as 2.74 g cm$^{-3}$ which agrees well with the observed value 2.72 g cm$^{-3}$.

## Discussion

### Distortion

Figure 1 shows the projection figure of upper and lower tetrahedral sheets. It has been known that, in the ideal figure of the structure of phlogopite, the dimension of the tetrahedral Si,Al sheet is larger than the octahedral $Mg_3$ sheet (RADOSLOVICH and NORRISH, 1962), and its tetrahedral rotation angle is obtained as 5.9 ° (MCCAULEY *et al.*, 1973).

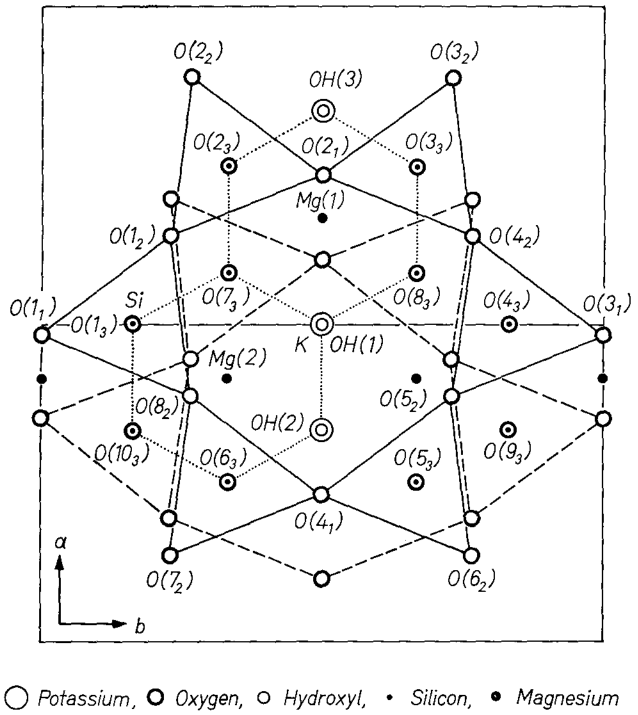

Fig. 1. Projection of a single layer of the synthesized $Mg^{IV}$ mica structure perpendicular to the layer. ——— Upper half tetrahedral layer, - - - - - Lower half tetrahedral layer, ······· Octahedral layer.

The ditrigonal distortion of the tetrahedral layer of the synthesized mica was obtained as 7.10 °, which is larger than that of phlogopite. The calculated value of $\alpha$ is obtained as 7.83 °, using the observed value of $b$ parameter (9.238 Å), and the calculated value (9.325 Å) obtained from the observed (Si,Mg)—O distance, 1.649 Å.

The tetrahedral rotation angle has been calculated by several ways. The angle can be obtained using the observed value of $b$ parameter and the distance of unrestrained tetrahedral sheets (Radoslovich and Norrish, 1962). The value of 6.83° was obtained by this method. Donnay *et al.* (1964) made a nomogram for predicting angle $\alpha$ from the measured value of $b$ parameter and estimated T—O distance. The present mica gave 7.82° by this method. The angle can be obtained from the ratio of the tetrahedral-octahedral layer misfit as shown in the following two equations: $b_t/b_o = 4D_t/3D_o$ and $b_o = b_t \cos \alpha$, where $b_t$ and $b_o$ are $b$ parameters of the tetrahedral and octahedral sheets respectively and $D_t$ and $D_o$ are tetrahedral and octahedral bond lengths respectively (McCauley and Newnham, 1971). The present sample gave 9.50° and 9.71° respectively by these equations. These calculated values are larger than the observed value. This discrepancy may be due to octahedral vacancy of the present mica.

Generally the calculated value of angle $\alpha$ is larger than the observed value. McCauley and Newnham (1971) showed that the discrepancy between the calculated and observed values of $\alpha$ shows a correlative relation to difference between the basal O—O distance, $d_1$, and the basal-apical O—O distance, $d_2$. In the present mica, calculated and observed $\alpha$ are close to each other, because the difference between $d_1$ and $d_2$ is extremely small (0.018 Å).

## Tetrahedral sheets

Observed (Si,Mg)—O distance is obtained as 1.649 Å in average with a standard deviation of 0.006 Å (Table 6). The mean Si—O bond length is obtained as 1.62 Å (Smith and Bailey, 1962), and the tetrahedral Mg—O distance is 1.955 Å (Khan, Bauer and Forbes, 1972). On the basis of these values, the distance, 1.649 Å, shows $8.5\,^0/_0$ substitution of Mg ions in the tetrahedral site, which is close to $7.6\,^0/_0$ substitution as found from the structural formula (Table 1).

Table 6. *Bond lengths in the tetrahedral sheet*
O(1) and O(2) are basal, O(3) is apical oxygen

| (Si,Mg)—O bond lengths | | O—O bond lengths | |
|---|---|---|---|
| (Si,Mg)—O($1_1$) | 1.668(17) Å | O($2_1$)—O($1_1$) | 2.701(17) Å |
| (Si,Mg)—O($2_1$) | 1.675(13) | O($2_8$)—O($1_1$) | 2.676(20) |
| (Si,Mg)—O($2_8$) | 1.636(13) | O($2_1$)—O($2_8$) | 2.681(19) |
| (Si,Mg)—O($3_1$) | 1.616(6) | O($3_1$)—O($1_1$) | 2.718(12) |
| | | O($3_1$)—O($2_1$) | 2.703(19) |
| | | O($3_1$)—O($2_8$) | 2.674(23) |
| Average | 1.649(6) Å | Average | 2.692(7) Å |

Bridging (Si,Mg)—O distance is 1.660 Å in mean and non-bridging distance (silicon to apical oxygen) is 1.616 Å. A cause to give rise to a shorter non-bridging distance than bridging one was explained by CRUICKSHANK (1961) with *d*-*p*-*π* bonding theory. The non-bridging distance of the present mica (1.615 Å) is longer than that of polylithionite (1.564 Å) reported by TAKEDA and BURNHAM (1969). This increase of the distance in the present synthesized mica is due to Mg ions substituting the tetrahedral sites.

### Interlayer sheets

Interlayer potassium ions are surrounded by six inner oxygen ions at 3.010 Å and outer six oxygen ions at 3.346 Å (Table 7). MCCAULEY and NEWNHAM (1971) showed the relation as $\Delta$ (Å) = 0.047 $\alpha$, where $\Delta$ is the difference between mean outer and inner interlayer cation-oxygen distances and $\alpha$ is the tetrahedral rotation angle. In the present mica, $\alpha$ is obtained as 7.14° from the difference as 0.336 Å, which is close to the observed value, 7.10°.

Table 7. *Bond lengths in the interlayer*

| Inner K—O distances | | Outer K—O distances | |
|---|---|---|---|
| K—O($1_2$) | 2.996(15) Å | K—O($1_4$) | 3.33(2) Å |
| K—O($2_8$) | 3.02(2) | K—O($2_1$) | 3.355(18) |
| Average | 3.010(7) Å | Average | 3.346(8) Å |

### Octahedral sheets

The mean ratio of shared and unshared edges of the octahedral sheet is obtained as 0.92 in the present mica, which agrees with the ratio 0.92 obtained from talc (Table 8). The same ratio compared with talc shows that the octahedral layer of this mica was not flattened by potassium.

### Origin of $Mg^{IV}$ mica

The alteration of talc into the $Mg^{IV}$ mica may be given as
$Mg_6Si_8O_{20}(OH)_4 + 2K^+ = K_2Mg_{5.50}(Si_{7.50}Mg_{0.50})O_{20}(OH)_4 + 0.5\ Si^{4+}$.
The equilibrium constant may be related only by the ratio of activities of K and Si ions. The similar equation may be constructed in the case of the reaction of tremolite and potassium carbonate. When we used the hornblende as a starting material, we could not obtain the $Mg^{IV}$ mica (TATEYAMA *et al.*, 1972). $Mg^{IV}$ mica may be stable under Al-free hydrothermal conditions only.

Table 8. *Bond lengths in the octahedral sheet*

| Mg(1)—O bond lengths | | Mg(2)—O bond lengths | |
|---|---|---|---|
| Mg(1)—O($3_2$) | 2.103(15) Å | Mg(2)—O($3_1$) | 2.095(18) Å |
| Mg(1)—OH(1) | 2.043(10) | Mg(2)—O($3_7$) | 2.103(15) |
| | | Mg(2)—OH(1) | 2.084(16) |
| Average | 2.062(7) Å | Average | 2.094(6) Å |
| **Unshared O—O bond lengths** | | | |
| Around Mg(1) site | | Around Mg(2) site | |
| O($3_2$)—O($3_3$) | 3.082(15) Å | O($3_1$)—O($3_6$) | 3.07(2) Å |
| O($3_2$)—OH(1) | 3.050(21) | O($3_6$)—OH(1) | 3.100(15) |
| | | O($3_1$)—OH(1) | 3.078(4) |
| Average | 3.061(8) Å | Average | 3.083(5) Å |
| **Shared O—O bond lengths** | | | |
| Around Mg(1) site | | Around Mg(2) site | |
| O($3_2$)—O($3_7$) | 2.862(15) Å | O($3_1$)—O($3_{10}$) | 2.862(15) Å |
| O($3_7$)—OH(1) | 2.809(17) | O($3_1$)—O($3_7$) | 2.87(2) |
| | | O($3_7$)—OH(1) | 2.809(17) |
| | | OH(1)—OH(2) | 2.793(15) |
| Average | 2.826(6) Å | Average | 2.835(7) Å |

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