THE CRYSTAL STRUCTURE OF MOSKVINITE-(Y), Na₂K (Y,REE) [Si₆O₁₅], A NEW SILICATE MINERAL WITH [Si₆O₁₅] THREE-MEMBERED DOUBLE RINGS FROM THE DARA-I-PIOZ MORaines, TIEN-SHAN MOUNTAINS, TAJIKISTAN

ELENA SOKOLOVA § AND FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

ATALI A. AGAKHANOV AND LEONID A. PAUTOV

Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow 117071, Russia

ABSTRACT

The crystal structure of moskvinite-(Y), ideally Na₂K (Y,REE) [Si₆O₁₅], from the moraine of the Dara-i-Pioz glacier, the Alai mountain range, Tien-Shan mountains, northern Tajikistan, a 10.623(2), b 14.970(2), c 8.553(1) Å, V 1359.8(4) Å³, space group Ibmm, Z = 4, D (calc.) = 2.850 g.cm −3 , has been solved by direct methods and refined to an R₁ index of 1.7% based on 936 observed [F o ] > 4σ[F] unique reflections collected with single-crystal diffractometer with MoKα X-radiation. Electron-microprobe analysis gave the composition Na₂.06 K 0.95 (Y 0.77 Dy 0.09 Gd 0.04 Er 0.04 Ho 0.02 Sm 0.02 Nd 0.01 Tb 0.01 )/H9018 1.00 Si 6 O 15 based on 15 O apfu. In the crystal structure of Na₂K (Y,REE) [Si₆O₁₅], there are two tetrahedrally coordinated T sites occupied by Si with <Si–O> = 1.623 Å. The (SiO₄) tetrahedra form three-membered rings, [Si₃O₉], that link by sharing apical vertices to form a double-ring of the form [Si₆O₁₅]. There are two [6]-coordinated sites, one occupied by (Y 0.77 + REE 0.23 ) with <(Y,REE)–O> = 2.255 Å, and the other occupied by Na with <Na–O> = 2.438 Å. There is a [10]-coordinated site occupied by K with <K–O> = 3.062 Å. The (Y,REE)O₁₀ and (NaO₆) octahedra share common edges to form sheets parallel to (010); these sheets connect through [Si₆O₁₅] double-rings to form a framework. Channels extend along [001] and contain K. The topology of the Na₂K Y [Si₆O₁₅] framework is identical to that of synthetic Na₃Y [Si₆O₁₅], but the arrangement of the channel cations is different. The crystal structures of double-ring silicates and [Si₆O₁₈]-chain structures are discussed.

Keywords: moskvinite-(Y), Y-silicate, crystal structure, [Si₆O₁₅] double ring, Dara-i-Pioz, Tajikistan.

SOMMAIRE

Nous avons résolu la structure cristalline de la moskvinite-(Y), dont la composition idéale est Na₂K (Y,REE) [Si₆O₁₅], provenant d’une moraine du glacier Dara-i-Pioz, dans la chaîne Alai des montagnes Tien-Shan, dans le nord du Tajikistan, a 10.623(2), b 14.970(2), c 8.553(1) Å, V 1359.8(4) Å³, groupe spatial Ibmm, Z = 4, D (calc.) = 2.850 g.cm −3 , par méthodes directes; la structure a été affinée jusqu’à un résidu R₁ de 1.7% en utilisant 936 réflexions uniques observées [F o ] > 4σ[F], prélevées avec un diffractomètre pour monocristal et un rayonnement MoKα. Une analyse à la microsonde électronique a donné Na₂.06 K 0.95 (Y 0.77 Dy 0.09 Gd 0.04 Er 0.04 Ho 0.02 Sm 0.02 Nd 0.01 Tb 0.01 )/H9018 1.00 Si 6 O 15 sur une base de 15 atomes d’oxygène par unité formulaire. La structure de Na₂K (Y,REE) [Si₆O₁₅] contient deux sites T à coordination tétraédrique qui occupent le Si, avec <Si–O> = 1.623 Å. Les tétraédres (SiO₄) sont agencés en anneaux à trois membres, [Si₃O₉], liés par partage de vertex apical pour former un anneau double [Si₆O₁₅]. Il y a deux sites à coordination [6]; l’un d’eux contient (Y 0.77 + REE 0.23 ) avec <(Y,REE)–O> = 2.255 Å, et l’autre contient le Na avec <Na–O> = 2.438 Å. Il y a de plus un site à coordination [10] qui occupe le K, avec <K–O> = 3.062 Å. Les octaédres [(Y,REE)O₆] et (NaO₆) partagent des arêtes pour former des feuillets parallèles à (010); ces feuillets sont liés par les anneau doubles [Si₆O₁₅] pour former une trame. Des canaux le long de [001] contiennent le potassium. La topologie de la trame Na₂K Y [Si₆O₁₅] serait identique à celle du composé synthétique Na₃Y [Si₆O₁₅], mais l’agencement des cations occupant les canaux est différent. Nous discutons des structures cristallines de silicats à anneaux doubles et de structures à chaînes [Si₆O₁₈].

(Traduit par la Rédaction)

Mots-clés: moskvinite-(Y), silicate d’yttrium, structure cristalline, anneau doubles [Si₆O₁₅], Dara-i-Pioz, Tajikistan.

§ E-mail address: sokolova@ms.umanitoba.ca
INTRODUCTION

Moskvinite-(Y), Na₂K(Y,REE)[Si₆O₁₅]₃, is a new mineral species from the moraine of the Dara-I-Pioz glacier, Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan (Agakhanyan et al. 2003). This is the first occurrence of the [Si₆O₁₅]₃⁻ double-ring in a structure of a mineral. Moskvinite-(Y) is the sixth silicate with a double ring [Si₆O₁₅]₃⁻ to be described from the Dara-I-Pioz moraine.

There are two types of double rings of tetrahedra previously known for silicates. Four-membered double rings [Si₈O₂₀] occur in the 18 minerals of the milar fragment of dimensions 0.04 mm. K(Y) were collected with a Siemens automated diffractometer with MoKα X-radiation from an irregular fragment of dimensions 0.04 × 0.06 × 0.06 mm. Twenty reflections over the range 7.6° ≤ 2θ ≤ 21.6° were centered, and the unit-cell dimensions (Table 2) were refined by least-squares from the resultant setting angles. To relate the moskvinite-(Y) structure to the previously reported structure of synthetic Na₂K(Y)[Si₆O₁₅] (Haile et al. 1995), we used the same cell orientation: Ihmm. Intensity data were collected in 0–20 scan-mode at a fixed scan-rate of 1.0°2θ/min. A total of 1160 reflections with 0 ≤ h ≤ 14, 0 ≤ k ≤ 21, 12 ≤ l ≤ 12 for moskvinite-(Y) was measured over the range 4 ≤ 2θ ≤ 60.13°. Psi-scan data were measured on 10 reflections out to 60°2θ at increments of 5° about the diffraction vector, and an absorption correction, with the crystal modeled as a triaxial ellipsoid, reduced R(azimuthal) from 3.8 to 1.7%. The data were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors; of the 1099 unique reflections, 936 were considered as observed (l|F)| ≥ 4σl).

STRUCTURE SOLUTION AND REFINEMENT

On the basis of 936 unique observed reflections, the crystal structure of moskvinite-(Y) was solved and refined with the Bruker SHELXTL Version 5 system of programs to R₁ = 1.7% and a GoF of 0.982 for a total of 71 refined parameters. Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). R indices are of the form given in Table 2, and are expressed as percentages. Site occupancies for the A, Na, K sites were refined with the scattering curves of Y, Na and K.

Atom positions and displacement parameters for moskvinite-(Y) are given in Table 3, selected interatomic distances in Table 4, and bond valences in Table 5. Observed and calculated structure-factors are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

| TABLE 1. RESULTS OF CHEMICAL ANALYSIS (W.T.%) AND FORMULA UNIT (apfu) FOR MOSKVINITE-(Y) |
|-----------------------------|-----------------------------|-----------------------------|
| SiO₂                      | 60.34                     | Si                         | 6.00                     |
| Na₂O₇                    | 10.66                     | Na                         | 2.06                     |
| K₂O                      | 7.50                      | Y                           | 0.95                     |
| Y₂O₁₃                   | 14.63                     | Sm                         | 0.54                     |
| Na₂O₁₂                   | 0.29                      | K                           | 0.95                     |
| Gd₂O₈                   | 0.54                      | Tb                          | 0.43                     |
| Tb₂O₇                   | 1.13                      | Dy                          | 0.43                     |
| Dy₂O₁₃                   | 2.76                      | Ho                          | 0.06                     |
| Ho₂O₁₃                   | 0.66                      | Er                          | 0.04                     |
| Er₂O₁₃                   | 1.17                      | Total                       | 100.13                   |
|                          |                           | Ho                          | 0.02                     |
|                          |                           | Er                          | 0.04                     |
|                          |                           | Σ                           | 1.00                     |
Cation coordination

There are two Si sites, each fully occupied by Si and coordinated by a tetrahedral array of O atoms with a \( <Si-O> \) distance of 1.623 Å. The shortest Si–O distances, \( Si(1)–O(2) = 1.578(2) \) and \( Si(2)–O(3) = 1.572(1) \) Å, involve bonds to apical O atoms (Table 5), whereas all other O atoms are bonded to two Si atoms. These short Si–O distances involving bonds to apical O atoms are fairly common in double-ring silicates. For example, Sokolova & Pautov (1995) noted that in Li-bearing minerals of the milarite structure-type, the \( T(1)–O(3) \) bond varies from 1.577 to 1.594 Å. There is one A site coordinated by an octahedral array of O atoms with a \( <A-O> \) distance of 2.255 Å. The total refined scattering at the A site is 46.0(1) e/aa (electrons per formula unit), and the analogous scattering calculated from the unit formula (Table 1) is 45.1 e/aa. Thus the A-site population...
tion was assigned as Y_{0.77}REE_{0.23}, following the unit formula. There is one Na site coordinated by an octahedral array of O atoms with a <Na–O> distance of 2.438 Å. There is one [10]-coordinated K site fully occupied by K with a <K–O> distance of 3.062 Å.

**Structure topology**

One \{Si(1)O_4\} and two \{Si(2)O_4\} tetrahedra share corners to form an [Si_3O_9] ring in the (001) plane. This ring links to its mirror equivalent across the mirror plane parallel to (010) to form an [Si_6O_15] cage or double ring (Fig. 1a). The (NaO_6) octahedra share one pair of trans corners to form an [NaO_5] chain that extends in the c direction (Fig. 1b). These chains are linked in the a direction by (AO_6) octahedra; the latter share two edges with the two adjacent chains (Fig. 1c) to form a sheet of octahedra parallel to (010). A sheet of similar topology formed by [8]-coordinated Y-polyhedra was described for the crystal structure of kuliokite-(Y), Y_4Al_4Si_12O_30(OH)_2F_4 (Sokolova et al. 1986). These sheets are linked in the b direction by [Si_6O_15] double rings (Fig. 1b), forming a compositionally layered heteropolyhedral framework. The sheet of octahedra parallel to (010) has eight-membered rings of edge-sharing octahedra (Fig. 1c), and the [Si_6O_15] double rings link to the inner perimeter of this ring by corner- and edge-sharing between tetrahedra and octahedra. In the crystal structure of moskvinite-(Y), stacking of A–Na sheets and (Si_6O_15) units produces one-dimensional channels that extend along [001] (Fig. 2a) and contain the K sites. There is a pseudo-C-centered superlattice that is obeyed by the arrangement of A and Na polyhedra and K atoms, but not by the (Si_6O_15) units (Fig. 2a).

The topology of the moskvinite-(Y) framework is identical to that of synthetic Na_3 Y [Si_6O_15], a 10.468(2), b 15.247(1), c 8.385(1) Å, V 1338.3 Å³, space group Ibmm, Z = 4, (Fig. 2b) (Haile et al. 1995), but the arrangement of the channel cations is quite different (Fig. 2b).

**Arrangement of the channel cations**

Haile et al. (1995) suggested that synthetic Na_3 Y [Si_6O_15] might be a fast-ion conductor. Figures 3a and 3b show the arrangements of the channel cations in the crystal structures of moskvinite-(Y) and synthetic Na_3 Y [Si_6O_15]. The ordering of the alkali cations is different in each structure. The Na(2) atoms in synthetic Na_3

---

**TABLE 5. BOND-VALENCE* \(\langle vu\rangle\) TABLE FOR MOSKVINITE-(Y)**

<table>
<thead>
<tr>
<th>(\text{A})</th>
<th>(\text{K})</th>
<th>(\text{Na})</th>
<th>(\text{Si(1)})</th>
<th>(\text{Si(2)})</th>
<th>(\Sigma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>0.07^{+}\</td>
<td>0.93^{−}\</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(2)</td>
<td>0.56^{+}\</td>
<td>0.17^{−}\</td>
<td>0.13</td>
<td>2.03</td>
<td></td>
</tr>
<tr>
<td>O(3)</td>
<td>0.13^{−}\</td>
<td>0.94^{+}\</td>
<td>0.98</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>O(4)</td>
<td>0.17^{−}\</td>
<td>0.09^{+}\</td>
<td>0.97^{−}\</td>
<td>2.17</td>
<td></td>
</tr>
<tr>
<td>O(5)</td>
<td>0.52^{+}\</td>
<td>0.07^{−}\</td>
<td>0.20^{+}\</td>
<td>1.15</td>
<td>1.98</td>
</tr>
<tr>
<td>O(6)</td>
<td>1.01^{−}\</td>
<td>0.01^{+}\</td>
<td>2.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\Sigma)</td>
<td>3.12</td>
<td>0.88</td>
<td>1.12</td>
<td>4.03</td>
<td>4.03</td>
</tr>
</tbody>
</table>

* Bond-valence curves are from Brown & Altermatt (1985)

---

**FIG. 1.** Fragments of the crystal structure of moskvinite-(Y): (a) a double three-membered ring [Si_6O_15]; (b), (c) two sheets of octahedra connected by [Si_6O_15] groups, viewed along [100] and [010], respectively. (SiO_4) tetrahedra are purple, (NaO_6) octahedra are yellow, (AO_6) octahedra are pink.
THE CRYSTAL STRUCTURE OF MOSKVINITE-(Y)

Y[Si₆O₁₅] half-occupy the 8i site (x y ¼), where Na(2)–O distances range from 2.525 to 3.634 Å; there is only 1.201 Å between adjacent Na(2) sites, and the fact that the Na(2) site is (long-range) half-occupied suggests that hopping of Na from occupied to unoccupied Na(2) sites will easily occur. The arrangement of Na sites in the large channels through the framework (Fig. 3b) makes these channels possible pathways for migration of Na atoms. In the crystal structure of moskvinite-(Y), K atoms (completely) occupy the 4e site (x 0 ¼). The shortest K–K distance along the channel is 4.52 Å, and ionic conductivity involving K seems improbable.

Fig. 2. The crystal structures of (a) moskvinite-(Y), and (b) synthetic Na₃Y[Si₆O₁₅], both projected onto (001). Legend as in Figure 1 except for atoms in the channels extending along [001]: K atoms are shown as green circles, Na atoms are shown as yellow circles.

Fig. 3. The arrangements of K and Na atoms along the [001] channel in the crystal structure of (a) moskvinite-(Y), and (b) synthetic Na₃Y[Si₆O₁₅]. K, Na and O atoms are shown as green, yellow and white circles, respectively.

Related Minerals

With the discovery of moskvinite-(Y), there are now three pairs of single and double n-membered (n = 3, 4, 6) silicate rings known in minerals. Three-membered
rings occur in the crystal structures of benitoite, Ba Ti [Si$_3$O$_9$] (Fischer 1969) (Fig. 4a) and moskvinite-(Y), ideally Na$_2$ K Y [Si$_6$O$_{15}$] (Fig. 4b). Four-membered rings have been described for the crystal structures of taramellite, ideally Ba$_4$ Fe$^{3+}$ Ti$_2$ [B$_2$Si$_8$O$_{27}$] O$_2$ Cl$_2$ (Mazzi & Rossi 1980) (Fig. 4c), and steacyite, Th Na$_2$ K [Si$_8$O$_{20}$] (Richard & Perrault 1972) (Fig. 4d). The structures of beryl, Be$_3$ Al$_2$ [Si$_6$O$_{18}$] (Fig. 4e) and milarite, K Ca$_2$ Al Be$_2$ [Si$_{12}$O$_{30}$] (Hawthorne et al. 1991) (Fig. 4f) contain six-membered rings.

Fig. 4. Single and double $n$-membered silicate rings in minerals: $n = 3$: (a) benitoite and (b) moskvinite-(Y); $n = 4$: (c) taramellite and (d) steacyite; $n = 6$: (e) beryl and (f) milarite.

Minerals with [Si$_n$O$_{2.5n}$] double rings

Moskvinite-(Y) is the first mineral to contain double rings of the form [Si$_6$O$_{15}$], and it should be noted that this is the smallest possible double-ring of tetrahedra. There are twenty-four minerals that contain double rings of tetrahedra of the form [Si$_n$O$_{2.5n}$], where $n = 4$ and 6. The minerals of the steacyite group, e.g., turkestanite, ideally Th (CaNa) K [Si$_8$O$_{20}$] (H$_2$O)$_n$ (Kabalov et al. 1998), contain double four-membered rings: [Si$_4$O$_{10}$].
The minerals of the milarite group (Hawthorne et al. 1991, Hawthorne 2002), $A_2 B_2 C [T(2)] T(1)_{12} O_{30}$ (H$_2$O)$_x$, $A =$ Al, Fe$^{3+}$, Sn$^{4+}$, Mg, Fe$^{2+}$, Ca, Na, Y, REE; $B = Na$, (H$_2$O), $C =$ K, Na, Ba, $T(1) = Si$, Al; $T(2) = Li$, Be, B, Mg, Al, Si, Mn$^{2+}$, Zn; contain double six-membered rings: $[Si_{12}O_{30}]$. In the crystal structure of moskvinite-(Y), each $[Si_{6}O_{15}]$ unit is connected to three K atoms and each $[10]$-coordinated K atom is connected to three $[Si_{6}O_{15}]$ units in a ratio $[Si_{6}O_{15}] : K = 1 : 1$ (Fig. 5a). In the crystal structures of steacyite and turkestanite, the four-membered $[Si_{8}O_{20}]$ double-ring is connected to four $[12]$-coordinated K atoms and vice versa, with the ratio $[Si_{8}O_{20}] : K = 1 : 1$ (Fig. 5b). There are two types of linkages between six-membered $[Si_{12}O_{30}]$ double-rings and K atoms in the milarite structure-type. In shibkovite, ideally Ca$^{2+}$ ($K^{[0.63]} B_{0.37}$) K Zn$_3$ $[Si_{12}O_{30}]$, K can occur at the $[9]B$ and $[12]C$ sites (Sokolova et al. 1999). Figure 5c shows the linkage of $[9]$-coordinated K atoms with the $[Si_{12}O_{30}]$ units in a ratio 1 : 1. This type of linkage is similar to those shown in Figures 5a and 5b. A different linkage occurs where $[12]$-coordinated K atoms and $[Si_{12}O_{30}]$ units alternate along the $c$ direction (Fig. 5d). Shibkovite is the only mineral of the milarite group with K at the $[9]B$ and $[12]C$ sites. In most milarite-group minerals, the $B$ site is occupied by Na or (H$_2$O), and linkage of K atoms and $[Si_{12}O_{30}]$ units occurs only in the $c$ direction.

**Other minerals with $[Si_{6}O_{15}]$ units**

The minerals of the tuhualite group contain a silicate unit of the same stoichiometry as that in moskvinite-(Y): emeleusite, Na Na Li Fe$^{3+}$ $[Si_{6}O_{15}]$ (Upton et al. 1994).
1978), tuhualite, □ Na Fe\(^{2+}\) Fe\(^{3+}\) [Si\(_6\)O\(_{15}\)] (Merlino 1969), and zektzerite, □ Na Li Zr [Si\(_6\)O\(_{15}\)] (Ghose & Wan 1978). However, the [Si\(_6\)O\(_{15}\)] unit in these minerals is a silicate double-chain of the Sechser-Doppelkette type (Liebau 1985). An [SiO\(_3\)] chain of corner-sharing tetrahedra connects to an identical chain across a mirror plane by sharing corners (Ghose & Wan 1978), giving rise to a double chain: [Si\(_2\)O\(_5\)] \(\rightarrow\) [Si\(_6\)O\(_{15}\)]. This chain also occurs in the synthetic compound Na\(_2\)Mg\(_2\) [Si\(_6\)O\(_{15}\)] (Cradwick & Taylor 1972).

ACKNOWLEDGEMENTS

We thank Tonči Balić-Zunić, Mark Welch and Associate Editor Ole Johnsen for their comments, and Editor Bob Martin for his indelible emendations. FCH was supported by a Canada Research Chair and Major Equipment, Discovery and Major Facilities Access grants from the Natural Sciences and Engineering Research Council of Canada.

REFERENCES


Received November 3, 2002, revised manuscript accepted March 4, 2003.