

**THE CRYSTAL STRUCTURE OF MOSKVINITE-(Y), Na<sub>2</sub> K (Y,REE) [Si<sub>6</sub>O<sub>15</sub>],  
A NEW SILICATE MINERAL WITH [Si<sub>6</sub>O<sub>15</sub>] THREE-MEMBERED DOUBLE RINGS  
FROM THE DARA-I-PIOZ MORAINÉ, TIEN-SHAN MOUNTAINS, TAJIKISTAN**

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ABSTRACT

The crystal structure of moskvinite-(Y), ideally Na<sub>2</sub> K (Y,REE) [Si<sub>6</sub>O<sub>15</sub>], 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) Å<sup>3</sup>, space group *Ibmm*, *Z* = 4, *D* (calc.) = 2.850 g.cm<sup>-3</sup>, has been solved by direct methods and refined to an *R*<sub>1</sub> index of 1.7% based on 936 observed [ $|F_o| > 4\sigma F$ ] unique reflections collected with single-crystal diffractometer with MoK $\alpha$  X-radiation. Electron-microprobe analysis gave the composition Na<sub>2.06</sub> K<sub>0.95</sub> (Y<sub>0.77</sub> Dy<sub>0.09</sub> Gd<sub>0.04</sub> Er<sub>0.04</sub> Ho<sub>0.02</sub> Sm<sub>0.02</sub> Nd<sub>0.01</sub> Tb<sub>0.01</sub>) $\Sigma$ 1.00 Si<sub>6</sub> O<sub>15</sub> based on 15 O *apfu*. In the crystal structure of Na<sub>2</sub> K (Y,REE) [Si<sub>6</sub>O<sub>15</sub>], there are two tetrahedrally coordinated *T* sites occupied by Si with  $\langle Si-O \rangle = 1.623$  Å. The (SiO<sub>4</sub>) tetrahedra form three-membered rings, [Si<sub>3</sub>O<sub>9</sub>], that link by sharing apical vertices to form a double-ring of the form [Si<sub>6</sub>O<sub>15</sub>]. There are two [6]-coordinated sites, one occupied by (Y<sub>0.77</sub> + REE<sub>0.23</sub>) with  $\langle (Y,REE)-O \rangle = 2.255$  Å, and the other occupied by Na with  $\langle Na-O \rangle = 2.438$  Å. There is a [10]-coordinated site occupied by K with  $\langle K-O \rangle = 3.062$  Å. The {(Y,REE)O<sub>6</sub>} and (NaO<sub>6</sub>) octahedra share common edges to form sheets parallel to (010); these sheets connect through [Si<sub>6</sub>O<sub>15</sub>] double-rings to form a framework. Channels extend along [001] and contain K. The topology of the Na<sub>2</sub> K Y [Si<sub>6</sub>O<sub>15</sub>] framework is identical to that of synthetic Na<sub>3</sub> Y [Si<sub>6</sub>O<sub>15</sub>], but the arrangement of the channel cations is different. The crystal structures of double-ring silicates and [Si<sub>6</sub>O<sub>18</sub>]-chain structures are discussed.

*Keywords:* moskvinite-(Y), Y-silicate, crystal structure, [Si<sub>6</sub>O<sub>15</sub>] double ring, Dara-i-Pioz, Tajikistan.

SOMMAIRE

Nous avons résolu la structure cristalline de la moskvinite-(Y), dont la composition idéale est Na<sub>2</sub> K (Y,REE) [Si<sub>6</sub>O<sub>15</sub>], 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) Å<sup>3</sup>, groupe spatial *Ibmm*, *Z* = 4, *D* (calc.) = 2.850 g.cm<sup>-3</sup>, par méthodes directes; la structure a été affinée jusqu'à un résidu *R*<sub>1</sub> de 1.7% en utilisant 936 réflexions uniques observées [ $|F_o| > 4\sigma F$ ], prélevées avec un diffractomètre pour monocristal et un rayonnement MoK $\alpha$ . Une analyse à la microsonde électronique a donné Na<sub>2.06</sub> K<sub>0.95</sub> (Y<sub>0.77</sub> Dy<sub>0.09</sub> Gd<sub>0.04</sub> Er<sub>0.04</sub> Ho<sub>0.02</sub> Sm<sub>0.02</sub> Nd<sub>0.01</sub> Tb<sub>0.01</sub>) $\Sigma$ 1.00 Si<sub>6</sub> O<sub>15</sub> sur une base de 15 atomes d'oxygène par unité formulaire. La structure de Na<sub>2</sub> K (Y,REE) [Si<sub>6</sub>O<sub>15</sub>] contient deux sites *T* à coordinence tétraédrique qu'occupe le Si, avec  $\langle Si-O \rangle = 1.623$  Å. Les tétraèdres (SiO<sub>4</sub>) sont agencés en anneaux à trois membres, [Si<sub>3</sub>O<sub>9</sub>], liés par partage de vertex apical pour former un anneau double [Si<sub>6</sub>O<sub>15</sub>]. Il y a deux sites à coordinence [6]; l'un d'eux contient (Y<sub>0.77</sub> + REE<sub>0.23</sub>), avec  $\langle (Y,REE)-O \rangle = 2.255$  Å, et l'autre contient le Na, avec  $\langle Na-O \rangle = 2.438$  Å. Il y a de plus un site à coordinence [10] qu'occupe le K, avec  $\langle K-O \rangle = 3.062$  Å. Les octaèdres {(Y,REE)O<sub>6</sub>} et (NaO<sub>6</sub>) partagent des arêtes pour former des feuillets parallèles à (010); ces feuillets sont liés par les anneaux doubles [Si<sub>6</sub>O<sub>15</sub>] pour former une trame. Des canaux le long de [001] contiennent le potassium. La topologie de la trame Na<sub>2</sub> K Y [Si<sub>6</sub>O<sub>15</sub>] serait identique à celle du composé synthétique Na<sub>3</sub> Y [Si<sub>6</sub>O<sub>15</sub>], mais l'agencement des cations occupant les canaux est différent. Nous discutons des structures cristallines de silicates à anneaux doubles et de structures à chaînes [Si<sub>6</sub>O<sub>18</sub>].

(Traduit par la Rédaction)

*Mots-clés:* moskvinite-(Y), silicate d'yttrium, structure cristalline, anneaux doubles [Si<sub>6</sub>O<sub>15</sub>], Dara-i-Pioz, Tajikistan.

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## INTRODUCTION

Moskvinite-(Y),  $\text{Na}_2\text{K}(\text{Y},\text{REE})[\text{Si}_6\text{O}_{15}]$ , is a new mineral species from the moraine of the Dara-i-Pioz glacier, Alai mountain ridge, Tien-Shan Mountains, northern Tajikistan (Agakhanov *et al.* 2003). This is the first occurrence of the  $[\text{Si}_6\text{O}_{15}]^{6-}$  double-ring in a structure of a mineral. Moskvinite-(Y) is the sixth silicate with a double ring  $[\text{Si}_n\text{O}_{2.5n}]$  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  $[\text{Si}_8\text{O}_{20}]$  occur in three minerals with the general formula  $^{[8]}A^{[8]}B_2^{[12]}C[\text{Si}_8\text{O}_{20}](\text{H}_2\text{O})_n$ , where  $A = \text{Th}, \text{REE}$ ;  $B = \text{Ca}, \text{Na}$ ;  $C = \text{K}, \square$ . They are steacyite,  $\text{Th}(\text{Na},\text{Ca})_2(\text{K}_{1-x}\square_x)\text{Si}_8\text{O}_{20}(\text{H}_2\text{O})_n$  (Richard & Perrault 1972, Perrault & Szymański 1982), iraqite-(La),  $\text{REE}(\text{Na},\text{Ca})_2(\text{K}_{1-x}\square_x)\text{Si}_8\text{O}_{20}(\text{H}_2\text{O})_n$  (Livingstone *et al.* 1976), and turkestanite,  $\text{Th}(\text{Ca},\text{Na})_2(\text{K}_{1-x}\square_x)\text{Si}_8\text{O}_{20}(\text{H}_2\text{O})_n$  (Kabalov *et al.* 1998); the crystal structure of iraqite-(La) is still unknown. Six-membered double-rings, ideally  $[\text{Si}_{12}\text{O}_{30}]$ , occur in the 18 minerals of the milarite group, with the general formula  $^{[6]}A_2^{[9]}B_2^{[12]}C^{[18]}D^{[4]}T(2)_3^{[4]}T(1)_{12}\text{O}_{30}$ , where  $T(1) = \text{Si}, \text{Al}$ ;  $T(2) = \text{Li}, \text{Be}, \text{B}, \text{Mg}, \text{Al}, \text{Si}, \text{Mn}^{2+}, \text{Zn}$ ;  $A = \text{Al}, \text{Fe}^{3+}, \text{Sn}^{4+}, \text{Mg}, \text{Zr}, \text{Fe}^{2+}, \text{Ca}, \text{Na}, \text{Y}, \text{REE}$ ;  $B = \text{Na}, \text{H}_2\text{O}, \text{K}, \square$ ;  $C = \text{K}, \text{Na}, \text{Ba}, \square$ ;  $D = \square$  (Forbes *et al.* 1972, Hawthorne *et al.* 1991). Here we report the crystal structure and crystal chemistry of moskvinite-(Y).

## ELECTRON-MICROPROBE ANALYSIS

The chemical composition of moskvinite-(Y) (Table 1) was established by wavelength-dispersion electron-microprobe analysis using a JXA-733 instrument operating at 20 kV and 20 nA. Standards were as follows: microcline USNM 143966 (Si, K), synthetic  $\text{Y}_2\text{O}_3$  (Y), synthetic Na (Al,Fe)  $\text{Si}_2\text{O}_6$  (Na) (USN standards from the Smithsonian Museum, Washington, USA). Concentrations of the rare-earth elements (REE) were determined titrimetrically after chromatographic partition. On the basis of 15 O *apfu* (atoms per formula unit), the following chemical formula for moskvinite-(Y) was obtained:  $\text{Na}_{2.06}\text{K}_{0.95}(\text{Y}_{0.77}\text{Dy}_{0.09}\text{Gd}_{0.04}\text{Er}_{0.04}\text{Ho}_{0.02}\text{Sm}_{0.02}\text{Nd}_{0.01}\text{Tb}_{0.01})\text{Si}_6\text{O}_{15}$ , which approximates closely to  $\text{Na}_2\text{K}(\text{Y},\text{REE})[\text{Si}_6\text{O}_{15}]$ .

## COLLECTION OF X-RAY DATA

Single-crystal X-ray-diffraction data for moskvinite-(Y) were collected with a Siemens P4 automated diffractometer with  $\text{MoK}\alpha$  X-radiation from an irregular fragment of dimensions  $0.04 \times 0.06 \times 0.06$  mm. Twenty reflections over the range  $7.6 \leq 2\theta \leq 21.9^\circ$  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  $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$

(Haile *et al.* 1995), we used the same cell orientation: *Ibmm*. Intensity data were collected in  $0-2\theta$  scan-mode at a fixed scan-rate of  $1.0^\circ/2\theta/\text{min}$ . A total of 1160 reflections with  $0 \leq h \leq 14$ ,  $0 \leq k \leq 21$ ,  $12 \leq l \leq 12$  for moskvinite-(Y) was measured over the range  $4 \leq 2\theta \leq 60.13^\circ$ . Psi-scan data were measured on 10 reflections out to  $60^\circ 2\theta$  at increments of  $5^\circ$  about the diffraction vector, and an absorption correction, with the crystal modeled as a triaxial ellipsoid, reduced  $R(\text{azimuthal})$  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  $[|F_o| \geq 4\sigma F]$ .

## 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  $R_1 = 1.7\%$  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 and 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 (WT.%) AND FORMULA UNIT (*apfu*) FOR MOSKVINITE-(Y)

$\text{SiO}_2$	60.34	Si	6.00
$\text{Na}_2\text{O}$	10.66		
$\text{K}_2\text{O}$	7.50	Na	2.06
$\text{Y}_2\text{O}_3$	14.63		
$\text{Nd}_2\text{O}_3$	0.29	K	0.95
$\text{Sm}_2\text{O}_3$	0.54		
$\text{Gd}_2\text{O}_3$	1.13	Y	0.77
$\text{Tb}_2\text{O}_3$	0.43	Nd	0.01
$\text{Dy}_2\text{O}_3$	2.76	Sm	0.02
$\text{Ho}_2\text{O}_3$	0.66	Gd	0.04
$\text{Er}_2\text{O}_3$	1.17	Tb	0.01
Total	100.13	Dy	0.09
		Ho	0.02
		Er	0.04
		$\Sigma$	1.00

TABLE 2. MISCELLANEOUS CRYSTAL STRUCTURE REFINEMENT DATA FOR MOSKVINITE-(Y)

<i>a</i> (Å)	10.623(2)	Crystal size (mm)	0.04 x 0.06 x 0.06
<i>b</i>	14.970(2)	Radiation	MoK $\alpha$
<i>c</i>	8.553(1)	2 $\theta$ range for data collection (°)	4–60.13
<i>V</i> (Å <sup>3</sup> )	1359.8(4)	Total # of reflections	1160
Space group	<i>lbmm</i>	<i>R</i> (int) (%)	2.1
<i>Z</i>	4	Unique reflections	1099
Absorption coefficient (mm <sup>-1</sup> )	5.52	<i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i>	936
<i>D</i> (calc)	2.925 g/cm <sup>3</sup>	Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup> ; fixed weights proportional to 1/ $\sigma$ ( <i>F</i> <sub>o</sub> <sup>2</sup> )
<i>F</i> (000)	1160	Goodness of fit on <i>F</i> <sup>2</sup>	0.982
		Final <i>R</i> index	<i>R</i> <sub>1</sub> = 1.74
		[ <i>F</i> <sub>o</sub> > 4 $\sigma$ <i>F</i> ]	
		<i>R</i> index(all data)	<i>R</i> <sub>1</sub> = 2.25 <i>wR</i> <sub>2</sub> = 4.10

TABLE 3. ATOM COORDINATES AND DISPLACEMENT PARAMETERS FOR MOSKVINITE-(Y)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>eq</sub>
Y(1)	1/4	1/4	1/4	0.00714(13)	0.00699(13)	0.00624(12)	0	0	-0.00077(11)	0.00679(8)
K	0.43056(9)	0	1/4	0.0234(5)	0.0373(6)	0.0154(4)	0	0	0	0.0254(2)
Na	1/2	0.25636(7)	0	0.0168(5)	0.0167(5)	0.0197(5)	0	0.0051(4)	0	0.0178(2)
Si(1)	0.53384(6)	0.40003(5)	1/4	0.0083(3)	0.0093(3)	0.0108(3)	0	0	-0.0013(2)	0.00943(15)
Si(2)	0.22002(4)	0.39603(3)	-0.07776(6)	0.0100(2)	0.0091(2)	0.0089(2)	0.00111(18)	0.00047(16)	0.00008(16)	0.00934(12)
O(1)	0.15917(17)	0.37118(13)	-1/4	0.0116(9)	0.0192(10)	0.0107(8)	0	0	-0.0025(8)	0.0138(4)
O(2)	0.43311(17)	0.32256(12)	1/4	0.0109(8)	0.0123(9)	0.0154(9)	0	0	-0.0038(7)	0.0129(4)
O(3)	0.37260(11)	0.38915(9)	-0.09771(15)	0.0101(6)	0.0173(7)	0.0114(6)	0.0011(5)	0.0003(5)	0.0000(5)	0.0129(3)
O(4)	0.18101(17)	1/2	-0.0448(2)	0.0170(9)	0.0086(8)	0.0211(10)	0	0.0034(8)	0	0.0155(4)
O(5)	0.16655(12)	0.33667(9)	0.05854(15)	0.0139(6)	0.0143(6)	0.0127(6)	0.0050(5)	-0.0010(5)	-0.0012(5)	0.0136(3)
O(6)	0.4751(3)	1/2	1/4	0.0139(13)	0.0097(12)	0.0184(13)	0	0	0	0.0140(5)

## DESCRIPTION OF THE CRYSTAL STRUCTURE OF MOSKVINITE-(Y)

## 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) *epfu* (electrons per formula unit), and the analogous scattering calculated from the unit formula (Table 1) is 45.1 *epfu*. Thus the *A*-site popula-

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR MOSKVINITE-(Y)

A–O(2)	x2	2.228(2)	Si(1)–O(2)	1.578(2)
A–O(5)	x4	<u>2.269(1)</u>	Si(1)–O(3)	x2 1.646(1)
<A–O>		2.255	Si(1)–O(6)	<u>1.622(1)</u>
			<Si(1)–O>	1.623
K–O(1)	x2	3.101(2)		
K–O(3)	x4	3.118(1)	Si(2)–O(1)	1.651(1)
K–O(4)a,b	x2	2.786(2)	Si(2)–O(3)	1.633(1)
K–O(4)c,d	x2	<u>3.187(2)</u>	Si(2)–O(4)	1.635(1)
<K–O>		3.062	Si(2)–O(5)	<u>1.572(1)</u>
			<Si(2)–O>	1.623
Na–O(2)	x2	2.461(1)		
Na–O(5)	x2	2.307(1)	Si(2)–O(1)–Si(2)e	126.3(1)
Na–O(3)	x2	<u>2.546(2)</u>	Si(2)–O(4)–Si(2)f	144.3(1)
<Na–O>		2.438	Si(2)–O(3)–Si(1)g	132.50(09)
			Si(1)–O(6)–Si(1)h	134.7(2)
			<Si–O–Si>	134.5

a:  $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$ ; b:  $-x+\frac{1}{2}, y-\frac{1}{2}, z$ ; c:  $x+\frac{1}{2}, -y+\frac{1}{2}, -z$ ;  
d:  $x+\frac{1}{2}, y-\frac{1}{2}, z+\frac{1}{2}$ ; e:  $x, y, -z-\frac{1}{2}$ ; f:  $x, -y+1, z$ ; g:  $-x+1, y, z-\frac{1}{2}$ ;  
h:  $x, -y+1, -z+\frac{1}{2}$

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  $\langle Na-O \rangle$  distance of 2.438 Å. There is one [10]-coordinated  $K$  site fully occupied by K with a  $\langle K-O \rangle$  distance of 3.062 Å.

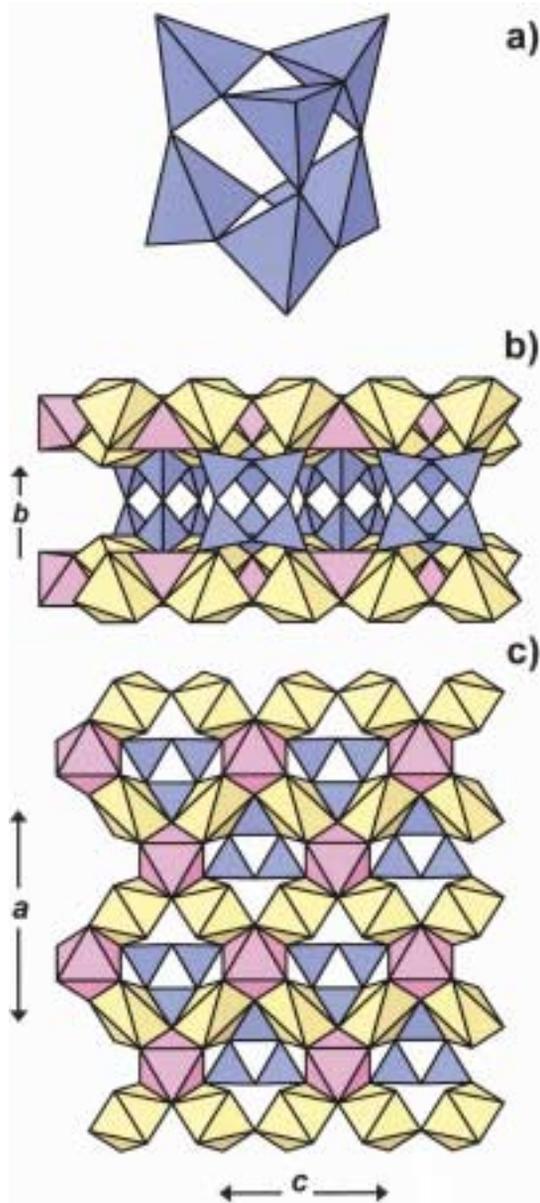


FIG. 1. Fragments of the crystal structure of moskvinitite-(Y): (a) a double three-membered ring  $[Si_6O_{15}]$ ; (b), (c) two sheets of octahedra connected by  $[Si_6O_{15}]$  groups, viewed along  $[100]$  and  $[010]$ , respectively.  $(SiO_4)$  tetrahedra are purple,  $(NaO_6)$  octahedra are yellow,  $(AO_6)$  octahedra are pink.

### 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),  $Y_4 Al [SiO_4]_2 (OH)_2 F_5$  (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 moskvinitite-(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 moskvinitite-(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 Å<sup>3</sup>, 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 moskvinitite-(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\* (vu) TABLE FOR MOSKVINITITE-(Y)

	A	K	Na	Si(1)	Si(2)	Σ
O(1)		0.07 <sup>x2</sup> <sub>1</sub>			0.93 <sup>x2</sup> <sub>-</sub>	2
O(2)	0.56 <sup>x2</sup> <sub>1</sub>		0.17 <sup>x2</sup> <sub>1-</sub>	0.13		2.03
O(3)			0.13 <sup>x2</sup> <sub>1</sub>	0.94 <sup>x2</sup> <sub>1</sub>	0.98	2.01
O(4)		0.17 <sup>x2</sup> <sub>1</sub> 0.06 <sup>x2</sup> <sub>1</sub>			0.97 <sup>x2</sup> <sub>-</sub>	2.17
O(5)	0.50 <sup>x4</sup> <sub>1</sub>	0.07 <sup>x4</sup> <sub>1</sub>	0.26 <sup>x2</sup> <sub>1</sub>		1.15	1.98
O(6)				1.01 <sup>x2</sup> <sub>-</sub>		2.02
Σ	3.12	0.88	1.12	4.03	4.03	

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

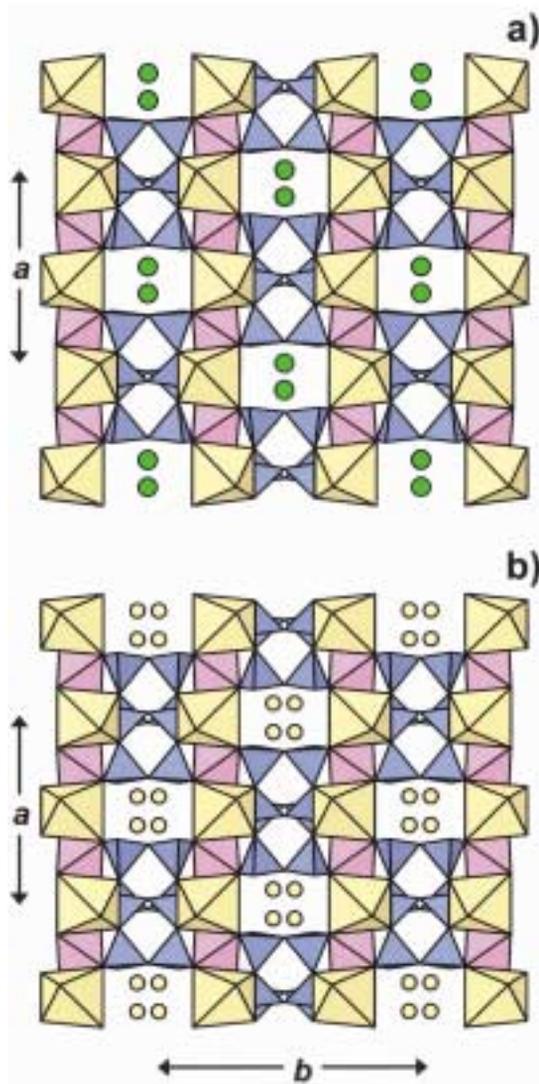


FIG. 2. The crystal structures of (a) moskvinit-(Y), and (b) synthetic  $\text{Na}_3\text{Y} [\text{Si}_6\text{O}_{15}]$ , both projected onto (001). Legend as in Figure 1 except for atoms in the channels extending along [001]: K atoms are shown as green circles, Na atoms are shown as yellow circles.

Y  $[\text{Si}_6\text{O}_{15}]$  half-occupy the  $8i$  site ( $x y \frac{1}{4}$ ), where  $\text{Na}(2)$ -O distances range from 2.525 to 3.634 Å; there is only 1.201 Å between adjacent  $\text{Na}(2)$  sites, and the fact that the  $\text{Na}(2)$  site is (long-range) half-occupied suggests that hopping of Na from occupied to unoccupied  $\text{Na}(2)$  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 moskvinit-(Y), K at-

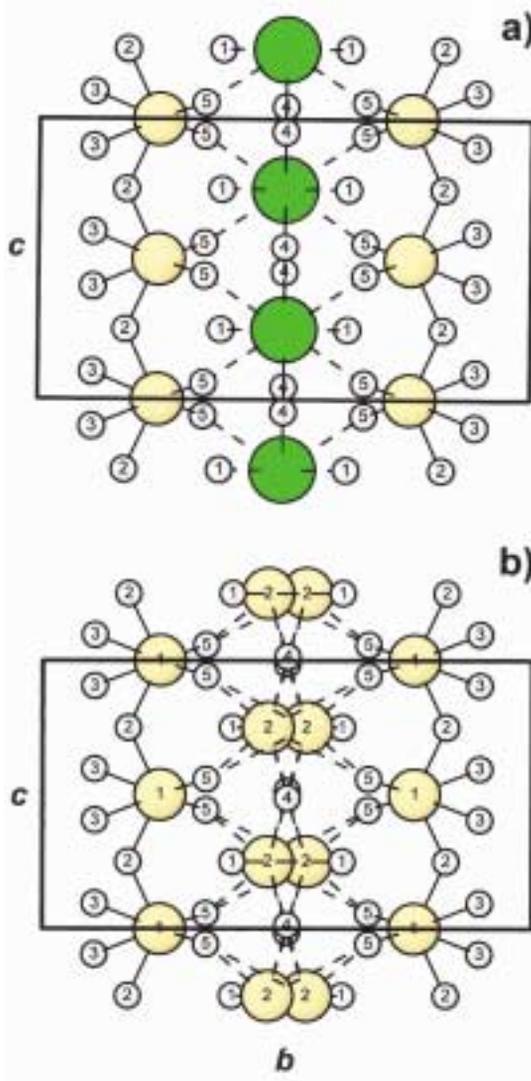


FIG. 3. The arrangements of K and Na atoms along the [001] channel in the crystal structure of (a) moskvinit-(Y), and (b) synthetic  $\text{Na}_3\text{Y} [\text{Si}_6\text{O}_{15}]$ . K, Na and O atoms are shown as green, yellow and white circles, respectively.

oms (completely) occupy the  $4e$  site ( $x 0 \frac{1}{4}$ ). The shortest K-K distance along the channel is 4.52 Å, and ionic conductivity involving K seems improbable.

#### RELATED MINERALS

With the discovery of moskvinit-(Y), there are now three pairs of single and double  $n$ -membered ( $n = 3, 4, 6$ ) silicate rings known in minerals. Three-membered

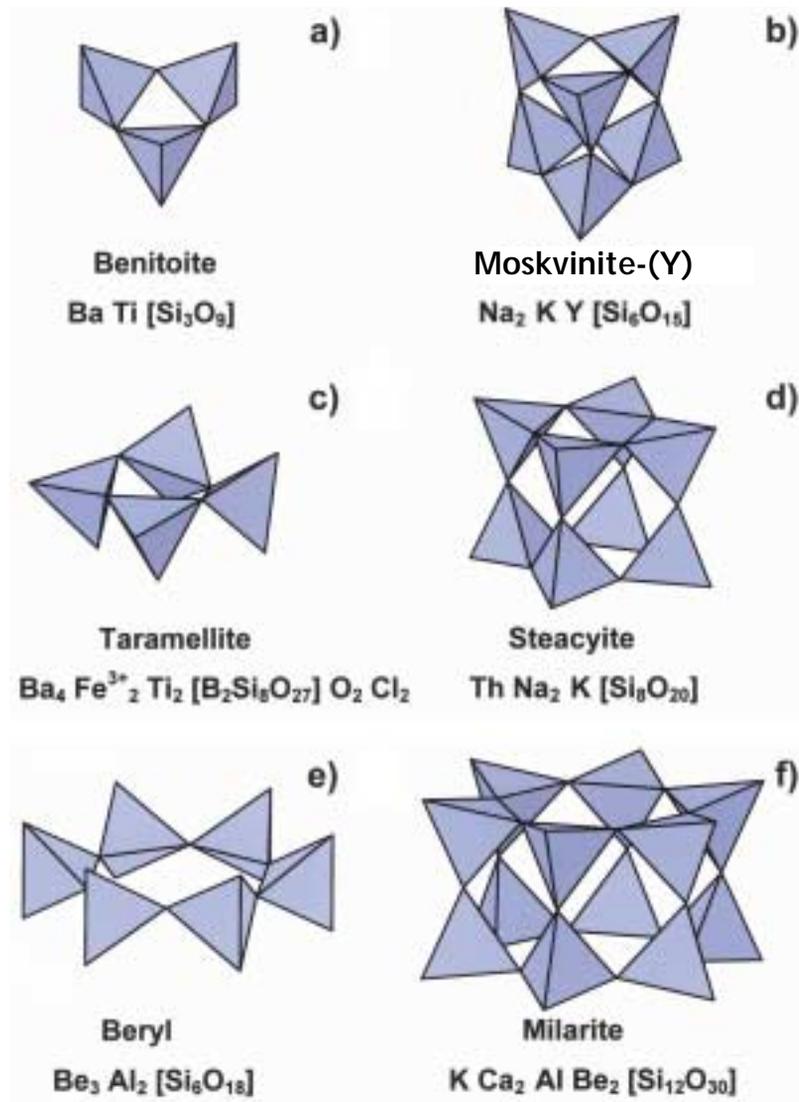


FIG. 4. Single and double  $n$ -membered silicate rings in minerals:  $n = 3$ : (a) benitoite and (b) moskvinitite-(Y);  $n = 4$ : (c) taramellite and (d) steacyite;  $n = 6$ : (e) beryl and (f) milarite.

rings occur in the crystal structures of benitoite, Ba Ti [Si<sub>3</sub>O<sub>9</sub>] (Fischer 1969) (Fig. 4a) and moskvinitite-(Y), ideally Na<sub>2</sub> K Y [Si<sub>6</sub>O<sub>15</sub>] (Fig. 4b). Four-membered rings have been described for the crystal structures of taramellite, ideally Ba<sub>4</sub> (Fe<sup>3+</sup><sub>2</sub>Ti<sub>2</sub>) [B<sub>2</sub>Si<sub>8</sub>O<sub>27</sub>] O<sub>2</sub> Cl<sub>2</sub> (Mazzi & Rossi 1980) (Fig. 4c), and steacyite, Th Na<sub>2</sub> K [Si<sub>8</sub>O<sub>20</sub>], (Richard & Perrault 1972) (Fig. 4d). The structures of beryl, Be<sub>3</sub> Al<sub>2</sub> [Si<sub>6</sub>O<sub>18</sub>], (Fig. 4e) and milarite, K Ca<sub>2</sub> Al Be<sub>2</sub> [Si<sub>12</sub>O<sub>30</sub>], (Hawthorne *et al.* 1991) (Fig. 4f) contain six-membered rings.

#### *Minerals with [Si<sub>n</sub>O<sub>2.5n</sub>] double rings*

Moskvinitite-(Y) is the first mineral to contain double rings of the form [Si<sub>6</sub>O<sub>15</sub>], 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<sub>n</sub>O<sub>2.5n</sub>], where  $n = 4$  and 6. The minerals of the steacyite group, *e.g.*, turkestanite, ideally Th (CaNa) K [Si<sub>8</sub>O<sub>20</sub>] (H<sub>2</sub>O)<sub>*n*</sub> (Kabalov *et al.* 1998), contain double four-membered rings: [Si<sub>8</sub>O<sub>20</sub>].

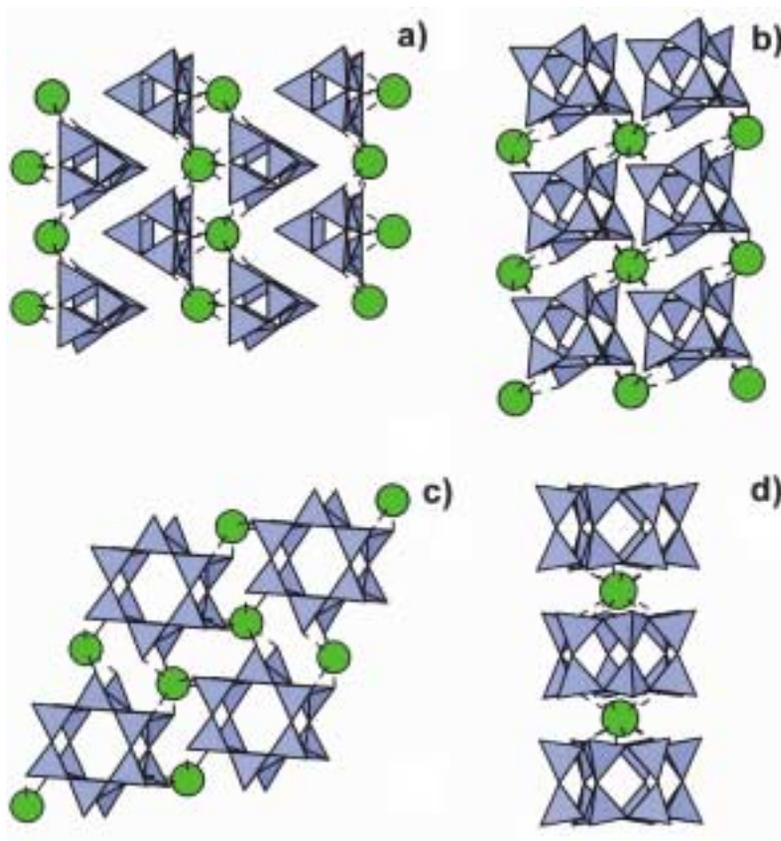


FIG. 5. Details of the connectivity of K atoms and  $[\text{SiO}_{2.5}]_n$  double rings: (a)  $[\text{Si}_6\text{O}_{15}]$  units and [10]-coordinated K atoms in the crystal structure of moskvinite-(Y), (b)  $[\text{Si}_8\text{O}_{20}]$  units and [12]-coordinated C (= K) atoms in the crystal structure of turkestanite, (c)  $[\text{Si}_{12}\text{O}_{30}]$  units and [9]-coordinated B (=  $\text{K}_{0.63} \square_{0.37}$ ) atoms in the crystal structure of shibkovite, and (d)  $[\text{Si}_{12}\text{O}_{30}]$  units and [12]-coordinated C (= K) atoms in the crystal structure of shibkovite.

The minerals of the milarite group (Hawthorne *et al.* 1991, Hawthorne 2002),  $A_2 B_2 C [T(2)_3 T(1)_{12} \text{O}_{30}] (\text{H}_2\text{O})_x$ ,  $A = \text{Al}, \text{Fe}^{3+}, \text{Sn}^{4+}, \text{Mg}, \text{Zr}, \text{Fe}^{2+}, \text{Ca}, \text{Na}, \text{Y}, \text{REE}$ ;  $B = \text{Na}, (\text{H}_2\text{O}), \square$ ;  $C = \text{K}, \text{Na}, \text{Ba}, \square$ ;  $T(1) = \text{Si}, \text{Al}$ ;  $T(2) = \text{Li}, \text{Be}, \text{B}, \text{Mg}, \text{Al}, \text{Si}, \text{Mn}^{2+}, \text{Zn}$ ; contain double six-membered rings:  $[\text{Si}_{12}\text{O}_{30}]$ .

In the crystal structure of moskvinite-(Y), each  $[\text{Si}_6\text{O}_{15}]$  unit is connected to three K atoms and each [10]-coordinated K atom is connected to three  $[\text{Si}_6\text{O}_{15}]$  units in a ratio  $(\text{Si}_6\text{O}_{15}) : \text{K} = 1 : 1$  (Fig. 5a). In the crystal structures of steacyite and turkestanite, the four-membered  $[\text{Si}_8\text{O}_{20}]$  double-ring is connected to four [12]-coordinated K atoms and *vice versa*, with the ratio  $[\text{Si}_8\text{O}_{20}] : \text{K} = 1 : 1$  (Fig. 5b). There are two types of linkages between six-membered  $[\text{Si}_{12}\text{O}_{30}]$  double-rings and K atoms in the milarite structure-type. In shibkovite, ideally  $\text{Ca}^{2+} (\text{K}\square) \text{K Zn}_3 [\text{Si}_{12}\text{O}_{30}]$ , 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  $[\text{Si}_{12}\text{O}_{30}]$  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  $[\text{Si}_{12}\text{O}_{30}]$  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  $(\text{H}_2\text{O})$ , and linkage of K atoms and  $[\text{Si}_{12}\text{O}_{30}]$  units occurs only in the *c* direction.

#### Other minerals with $[\text{Si}_6\text{O}_{15}]$ units

The minerals of the tuhualite group contain a silicate unit of the same stoichiometry as that in moskvinite-(Y): emeleusite,  $\text{Na Na Li Fe}^{3+} [\text{Si}_6\text{O}_{15}]$  (Upton *et al.*

1978), tuzualite,  $\square$  Na Fe<sup>2+</sup> Fe<sup>3+</sup> [Si<sub>6</sub>O<sub>15</sub>] (Merlino 1969), and zektzerite,  $\square$  Na Li Zr [Si<sub>6</sub>O<sub>15</sub>] (Ghose & Wan 1978). However, the [Si<sub>6</sub>O<sub>15</sub>] unit in these minerals is a silicate double-chain of the *Sechser-Doppelkette* type (Liebau 1985). An [SiO<sub>3</sub>] 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<sub>2</sub>O<sub>5</sub>] × 3 → [Si<sub>6</sub>O<sub>15</sub>]. This chain also occurs in the synthetic compound Na<sub>2</sub> Mg<sub>2</sub> [Si<sub>6</sub>O<sub>15</sub>] (Cradwick & Taylor 1972).

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