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$Cs[Si_3O_6(OH)]$ and $Rb[Si_2O_4(OH)]$: two novel phyllosilicates

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The crystal structures of two novel phyllosilicates with compositions $Cs[Si_3O_6(OH)]$ (caesium hydroxohexaoxotetraotrisilicate) and $Rb[Si_2O_4(OH)]$ (rubidium hydroxohexaoxotetraodisilicate) have been characterized by X-ray diffraction. The topology of the caesium phyllosilicate silica sheet consists of interconnected four- and six-membered rings and thus differs from all of the previously reported phyllosilicates. The topology of the rubidium phyllosilicate silica sheet consists of six-membered rings only, in boat conformations, resulting in a corrugated sheet similar to that observed in δ-$Na_2Si_2O_5$. Both of the title compounds exhibit the characteristic sandwich structure of sheet silicates, with the Cs atom ninefold coordinated and the Rb atom eightfold coordinated to the framework O atoms.

Comment

During our search for novel mixed-geometry (octahedral/tetrahedral metal oxide) open frameworks, we discovered two phyllosilicate by-products and subsequently altered the synthesis conditions in order to isolate these layered silicates. Both title compounds exhibit novel phyllosilicate structures. The rubidium compound, (II), is the only known high-mass alkali described by a six-membered-ring silica sheet, a characteristic reported to belong to low-mass alkali phyllosilicates (Dejong *et al.*, 1994). The caesium compound, (I), exhibits novel four- and six-membered-ring sheets, in which the six-membered rings adopt boat conformations. A structural study of these layered compounds may lead to a better understanding of the hydrothermal synthesis of octahedral/tetrahedral open frameworks, since a large number of reported mixed-geometry metal oxide frameworks exhibit alternating layers of silica sheets and octahedral metal oxide sheets (Ananias *et al.*, 2001; Rocha *et al.*, 1998). Furthermore, these structures have potential applications in ion-exchange and chemisorption processes (Da Fonseca *et al.*, 2000; Lagadic *et al.*, 2001; Pagnoux *et al.*, 1991). Preliminary experiments for $Rb[Si_2O_4(OH)]$, (II), are promising in this context.

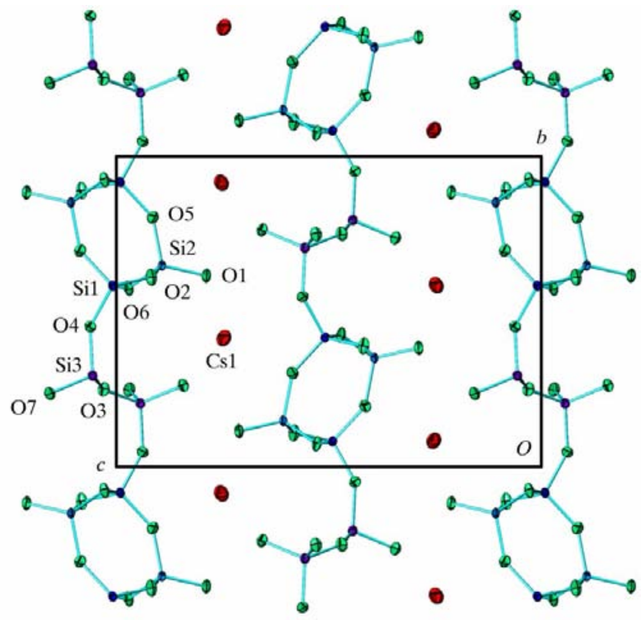

Figure 1
[100] view of the framework of (I), illustrating the layered character of this material. Si, O and Cs atoms are shown as light grey, black and medium grey circles, respectively.

Fig. 1 illustrates the sandwich structure of (I), clearly showing the Cs atoms residing between the silica sheets. The Cs atom is coordinated to nine neighboring O atoms, with Cs—O distances in the range 3.029 (4)–3.630 (4) Å. Two pendant O atoms propagate into the interlayer space, of which one must be protonated for the electroneutrality of the structure. No H atoms could be located in difference Fourier maps because of the large electron density associated with the Cs atom. However, the Si3—O7 bond length of 1.598 (4) Å agrees with the value reported for an Si—OH bond length in tetrahedral silicates with three bridging O atoms (Nyfeler & Armbruster, 1998). Fig. 2 illustrates the four- and six-membered-ring topology of the silica sheet, which is unique to phyllosilicates.

Fig. 3 illustrates the typical phyllosilicate sandwich structure of (II). The Rb atom occupies the interlayer space and is

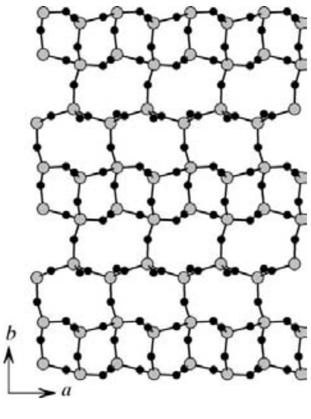

Figure 2
[001] view illustrating the four- and six-membered-ring topology of the phyllosilicate sheets in (I). Si and O atoms are shown as light grey and black circles, respectively. Cs atoms has been omitted for clarity.

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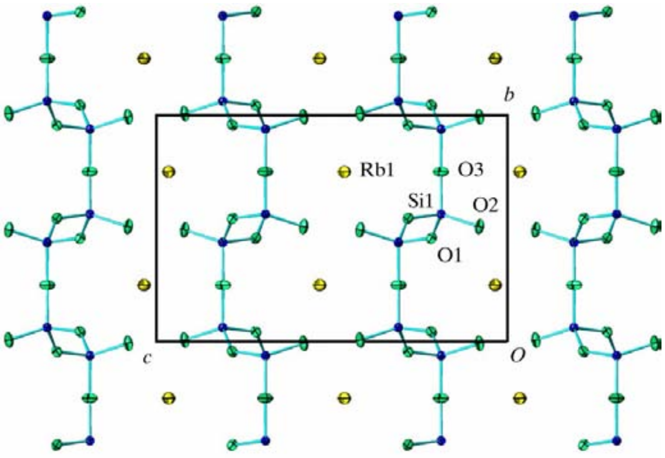

Figure 3
[100] view of the framework of (II), illustrating the layered character of this material. Si, O and Rb atoms are shown as light grey, black and medium grey circles, respectively.

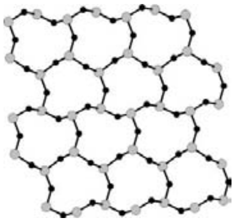

Figure 4
[001] view illustrating the six-membered-ring topology of the phyllosilicate sheets in (II). Si and O atoms are shown as light grey and black circles, respectively. Rb atoms has been omitted for clarity.

eightfold coordinated to neighboring O atoms, with Rb—O distances in the range 2.911 (2)–3.576 (4) Å. Again, no H atoms could be located in difference Fourier maps, although the presence of H atoms is required for the electroneutrality of the structure. The Si1—O2 bond length of 1.591 (2) Å is slightly shorter than that reported for a typical Si—OH bond length in this bonding situation, reflecting the fact that the O atom only requires protonation to a fractional occupancy of 0.5 (Nyfeler & Armbruster, 1998). Fig. 4 depicts the corrugated six-membered-ring topology of the silica sheet, which is very similar to the topology of δ-$Na_2Si_2O_5$ (Kahlenberg *et al.*, 1999). Compound (II) is the first example of a high-mass alkali phyllosilicate with such a topology, and this result may raise new questions concerning the molecular modeling of disilicate glasses from phyllosilicate structures (Nyfeler & Armbruster, 1998).

Experimental

$Cs[Si_3O_6(OH)]$ was prepared from tetramethoxysilane (1.477 g), caesium hydroxide (1.512 g), tetraethylammonium hydroxide (TEAOH, 0.326 g) and distilled water (6 ml), giving an $SiO_2/Cs_2O/$TEAOH/H_2O gel composition of 1:0.26:0.08:40. $Rb[Si_2O_4(OH)]$ was prepared from colloidal silica (Aldrich AS40, 0.627 g), rubidium hydroxide (2.086 g) and distilled water (9 ml), giving an $SiO_2/Rb_2O/H_2O$ gel composition of 1:1.95:120. Both reactions were carried out in Parr acid digestion bombs with 23 ml poly(tetrafluoroethylene) liners. All gels were prepared, mixed and aged for 1 h in the Teflon liners, which were generally half-filled. Both reactions were carried out at 493 K for a period of 5 d.

Compound (I)

Crystal data

$Cs[Si_3O_6(OH)]$
$M_r = 330.19$
Orthorhombic, $P2_12_12_1$
$a = 4.9163$ (9) Å
$b = 10.340$ (2) Å
$c = 14.136$ (3) Å
$V = 718.6$ (2) Å^3
$Z = 4$
$D_x = 3.052$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 192 reflections
$\theta = 5$–25°
$\mu = 5.64$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.22 × 0.04 × 0.02 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.370$, $T_{max} = 0.896$
5183 measured reflections

1670 independent reflections
1517 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 28.2°$
$h = -6 \rightarrow 6$
$k = -12 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R(F) = 0.033$
$wR(F^2) = 0.082$
$S = 0.93$
1670 reflections
101 parameters
H atom not located
$w = 1/[\sigma^2(F_o^2) + (0.0433P)^2 + 0.0545P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0221 (12)
Absolute structure: Flack (1983), 650 Friedel pairs
Flack parameter = 0.00 (3)

Compound (II)

Crystal data

$Rb[Si_2O_4(OH)]$
$M_r = 222.66$
Orthorhombic, *Pcmn*
$a = 4.8147$ (13) Å
$b = 8.267$ (2) Å
$c = 12.814$ (3) Å
$V = 510.0$ (2) Å^3
$Z = 4$
$D_x = 2.9$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 89 reflections
$\theta = 5$–25°
$\mu = 10.10$ mm^{-1}
$T = 293$ (2) K
Hexagonal, colorless
0.11 × 0.04 × 0.01 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.403$, $T_{max} = 0.906$
3401 measured reflections

647 independent reflections
559 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 28.2°$
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R(F) = 0.027$
$wR(F^2) = 0.080$
$S = 1.09$
647 reflections
40 parameters
H atom not located

$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 0.2002P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}

For both compounds, data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1030). Services for accessing these data are described at the back of the journal.

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