inorganic papers

Potassium sodium phyllosilicate, $K_{1.33}Na_{0.67}Si_2O_5$

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The two-dimensional network topology of the mixed alkali
title compound, $K_{1.33}Na_{0.67}Si_2O_5$, is found to differ from that
of the end-member compositions, $Na_2Si_2O_5$ and $K_2Si_2O_5$. The
network of the silicate sheet consists of rings with four, six and
eight SiO_4 tetrahedra. The cations are sandwiched between
the silicate sheets.

Comment

In previous papers, we have described the preparation and
structures of a number of crystalline alkali and mixed alkali
disilicates (phyllosilicates) with chemical formula $R_2O{\cdot}2SiO_2$
(R = Li, Na, K, Rb and Cs; de Jong *et al.*, 1994, 1996, 1998,
2000; Veldman *et al.*, 1995). Not all combinations of alkali
metals form mixed alkali disilicates at ambient pressure. The
impossible combinations are (Li,Na), (K,Rb), (K,Cs) and
(Rb,Cs) disilicates. Their cationic field strength difference is
too small according to a theory proposed by Dietzel (1983).

There are many reasons why the study of these materials is
useful. Our reason was to find an explanation for the variation
in hygroscopicity of mixed alkali disilicate glasses. These
glasses may be used as model compounds for dried soluble
silicates (Weldes & Lange, 1969), for which there was an
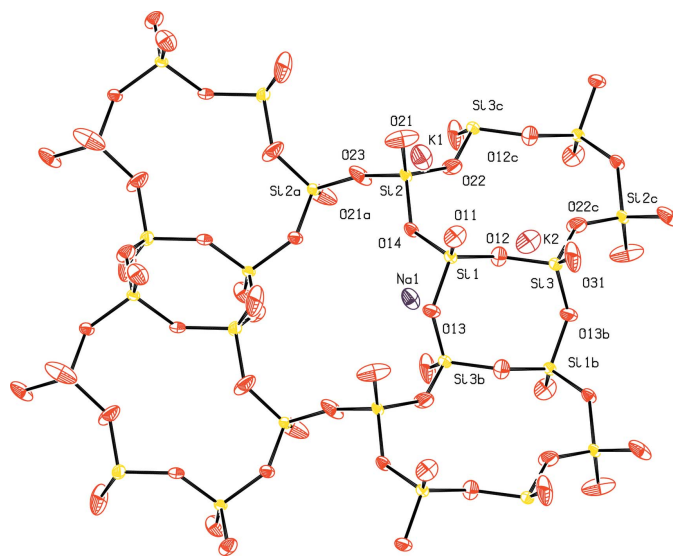industrial need to make them non-hygroscopic. Though

Figure 1
View of part of the Si_2O_5 two-dimensional network consisting of four-,
six- and eight-membered rings of SiO_4 tetrahedra and crystallographically
independent cations, along with the atom-numbering scheme. Displace-
ment ellipsoids are drawn at the 70% probability level. [Symmetry codes:
(a) $-x$, y, $-\frac{1}{2}-z$; (b) $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$; (c) $\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$.]

soluble silicates tend to have a lower alkali-to-silica ratio, we chose as a homologous the alkali disilicates. The advantage of this system is that it can form, next to glasses, crystalline disilicates, which have hygroscopicities similar to their glassy congeners. Such crystalline materials can of course be analyzed structurally as well as chemically in much more detail to discover the causes for the observed very large variations in hygroscopicity. Unfortunately, no obvious structure–hygroscopy relation was found.

From a crystal chemical perspective, these single and mixed alkali systems turned out to be surprisingly rich in network topologies. Though compositionally constrained to structures in which each tetrahedron contains three O atoms connected to two Si atoms, and one O atom connected to only one Si atom, they formed not only sheets but also three-dimensional networks and one-dimensional ribbons. One of the few remaining phases we synthesized in this system was the mixed (K,Na) disilicate structure, which has recently received renewed attention (Rakic & Kahlenberg, 2001; Rakic *et al.*, 2003*a*,*b*).

The title compound, $K_{1.33}Na_{0.67}Si_2O_5$, is a sheet silicate (Figs. 1 and 2) with four-, six- and eight-membered rings of SiO_4 tetrahedra. Na is five-coordinated and K six-coordinated by oxygen.

Experimental

The crystalline phase can be made without any special precaution by mixing K_2CO_3 (1 mol), Na_2CO_3 (1 mol) and SiO_2 (4 mol), calcining the mixture at 800 K to remove the CO_2, and melting the resulting $K_2O \cdot Na_2O \cdot 4SiO_2$ (m.p. 878 K; Kracek, 1932) mixture at 1000 K, followed by cooling at a rate of 0.5 K min^{-1}. Samples were immersed in petroleum jelly to prevent absorption of moisture.

Crystal data

$K_{1.33}Na_{0.67}Si_2O_5$
$M_r = 203.64$
Monoclinic, $C2/c$
$a = 19.6816 (15)$ Å
$b = 7.2656 (6)$ Å
$c = 12.5710 (15)$ Å
$\beta = 117.82 (1)°$
$V = 1589.9 (3)$ Å^3
$Z = 12$

$D_x = 2.552$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9 reflections
$\theta = 10–14°$
$\mu = 1.71$ mm^{-1}
$T = 150$ K
Block, colorless
$0.3 \times 0.3 \times 0.2$ mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
ω scans
Absorption correction: none
2841 measured reflections
1406 independent reflections
1094 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$

$\theta_{max} = 25°$
$h = -23 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -13 \rightarrow 14$
1 standard reflections
  frequency: 60 min
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.118$
$S = 1.09$
1406 reflections
123 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0465P)^2 + 11.2001P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
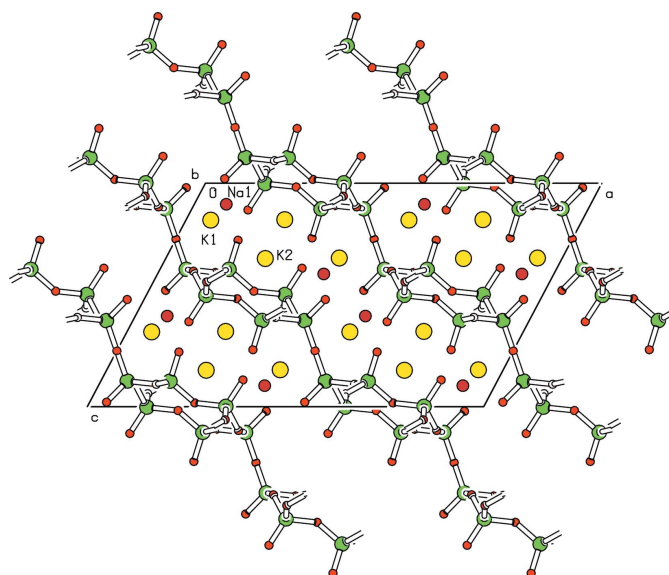$\Delta\rho_{min} = -0.92$ e Å^{-3}

Figure 2
Projection of the structure down the b axis, illustrating the layer structure with the cations sandwiched in between.

Table 1
Selected interatomic distances (Å).

Si1—O11	1.559 (4)	K1—O14^{iv}	2.904 (4)
Si1—O12	1.636 (5)	K1—O13^{iv}	3.353 (5)
Si1—O13	1.634 (5)	K1—O31^{v}	2.637 (5)
Si1—O14	1.650 (4)	K2—O11	2.614 (4)
Si2—O14	1.647 (4)	K2—O31	2.607 (5)
Si2—O21	1.550 (6)	K2—O12^{iv}	2.884 (4)
Si2—O22	1.620 (5)	K2—O22^{iv}	2.850 (5)
Si2—O23	1.6024 (16)	K2—O22^{vi}	2.980 (6)
Si3—O12	1.643 (4)	K2—O12^{vi}	3.127 (4)
Si3—O31	1.550 (4)	Na1—O11	2.495 (5)
Si3—O13^{i}	1.630 (5)	Na1—O13	2.702 (5)
Si3—O22^{ii}	1.638 (5)	Na1—O21^{vii}	2.356 (5)
K1—O11	2.563 (5)	Na1—O21^{iii}	2.271 (7)
K1—O21	2.562 (5)	Na1—O31^{vi}	2.291 (5)
K1—O14^{iii}	2.899 (5)		

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (iii) $-x, -y + 1, -z$; (iv) $x, -y + 1, +z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, +y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}, +y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x, y - 1, z$.

The displacement parameters of O23 were restrained to be approximately isotropic.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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