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Structure of $KLiSi_2O_5$ and the Hygroscopicity of Glassy Mixed Alkali Disilicates

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Abstract

$KLiSi_2O_5$, $M_r = 182.21$, $\lambda(\text{Mo}\,K\alpha) = 0.71073$ Å, 150 K, monoclinic, $P2_1$, $a = 5.9803\,(6)$, $b = 4.7996\,(6)$, $c = 8.1599\,(11)$ Å, $\beta = 93.477\,(10)^\circ$, $V = 233.78\,(5)$ Å^3, $\mu(\text{Mo}\,K\alpha) = 15.7\,\text{cm}^{-1}$, $Z = 2$, $F(000) = 180$, $D_x = 2.5885\,(6)\,\text{Mg}\,\text{m}^{-3}$, $R_1 = 0.0331$ for 1023 reflections with $I > 2.0\sigma(I)$, $wR_2 = 0.0864$ for all 1064 reflections. The crystal structure of potassium lithium phyllosilicate has been determined and the hygroscopicity of glassy single and mixed alkali disilicates has been measured. The potassium lithium phyllosilicate sheet topology is the same as that of lithium phyllosilicate, consisting of six-membered silica rings in a chair configuration. Li is fourfold oxygen coordinated by three non-bridging O and one bridging O, while K is sixfold oxygen coordinated by five non-bridging O and one bridging O. The K atoms are sandwiched between the $LiSi_2O_5$ layer. Crystalline and glassy lithium disilicate are not hygroscopic. Crystalline and glassy potassium disilicate are the most hygroscopic alkali disilicates known to date, whereas the mixed system, crystalline and glassy lithium potassium disilicate, is again not hygroscopic. Calculated valences for lithium potassium phyllosilicate do not provide a rationale for these observations.

1. Introduction

The crystal structures of eight alkali disilicates, designated as phyllosilicates (Liebau, 1985), stable and metastable $Li_2Si_2O_5$ (Liebau, 1961; Spek, Supèr & de Jong, 1996; Smith, Howie, West, Aragón-Piña & Villafuerte-Castrejon, 1990), α-, β-, ε-$Na_2Si_2O_5$ (Pant, 1968; Pant & Cruickshank, 1968; Fleet & Henderson, 1995), $Rb_2Si_2O_5$, $Cs_2Si_2O_5$, $Cs_{1.33}Li_{0.67}Si_2O_5$ (Veldman, Spek, Supèr & de Jong, 1995; de Jong, Slaats, Supèr, Veldman & Spek, 1994), and one alkaline earth phyllosilicate, $BaSi_2O_5$ (Hesse & Liebau, 1980), with an alkali or alkaline earth oxide to silica ratio of 0.5, are known. Some of these phyllosilicates are very susceptible to moisture absorbance from air, others not at all. In the course of studying these large variations in moisture adsorbance on glassy alkali disilicates we noted that all lithium-containing systems tend not to be hygroscopic. Searching for the cause of this phenomenon we have prepared some mixed lithium alkali phyllosilicates and determined their crystal structures.

After preparing a non-hygroscopic caesium lithium phyllosilicate and determining its crystal structure (Veldman, Spek, Supèr & de Jong, 1995) we set out to determine the crystal structure of potassium lithium phyllosilicate, hoping by inspection of its structure to find out why this compound is not hygroscopic. Our results show that the silica sheet in potassium lithium phyllosilicate is topologically equivalent to that of lithium phyllosilicate, but not to that of rubidium or caesium phyllosilicate, and that the role of Li in preventing hygroscopicity cannot be assessed from the calculation of the valences of the constituent atoms in this structure.

2. Experimental

We prepared crystalline potassium lithium phyllosilicate by programmed cooling from a $K_2O.Li_2O.4SiO_2$ composition melt. The melting temperature determined by DTA was 1095 K. Fused silicic acid and lithium potassium carbonates were decarbonated at 1073 K, molten at 1173 K and held at that temperature for 3 h, followed by programmed cooling to 973 K with a ramp of 0.7 K min^{-1} and a hold for ~28 h at that temperature. Optical inspection of the resulting large transparent crystals showed the characteristic blades of a phyllosilicate.

A specimen suitable for X-ray data collection was cut to the required shape and fixed on top of a Lindemann glass capillary. Data were collected on an

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Table 1. *Experimental details*

Crystal data	
Chemical formula	$KLiSi_2O_5$
Chemical formula weight	182.21
Cell setting	Monoclinic
Space group	$P2_1$
a (Å)	5.9803 (6)
b (Å)	4.7996 (6)
c (Å)	8.1599 (11)
β (°)	93.477 (10)
V (Å^3)	233.78 (5)
Z	2
D_x (Mg m^{-3})	2.5885 (6)
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	15
θ range (°)	10–16
μ (mm^{-1})	1.57
Temperature (K)	150
Crystal form	Plate
Crystal size (mm)	0.40 × 0.23 × 0.08
Crystal colour	Colourless
Data collection	
Diffractometer	Enraf–Nonius CAD-4T/RA
Data collection method	ω
Scan (°)	$0.98 + 0.35\tan\theta$
Horizontal and vertical aperture (mm)	3.0, 4.0
Reference reflections	$\bar{2}1\bar{5}$, $\bar{2}\bar{2}\bar{2}$, $\bar{3}\bar{2}0$
Absorption correction	None
No. of measured reflections	2376
No. of independent reflections	1064
No. of observed reflections	1023
Criterion for observed reflections	$I > 2.0\sigma(I)$
$R_{\rm int}$	0.0828
$\theta_{\rm max}$ (°)	27.5
Range of h, k, l	$-7 \rightarrow h \rightarrow 7$ $-6 \rightarrow k \rightarrow 6$ $-10 \rightarrow l \rightarrow 10$
No. of standard reflections	3
Frequency of standard reflections (min)	60
Intensity decay (%)	2
Refinement	
Refinement on	F^2
$R^*[I > 2\sigma(I)]$	0.0331
wR_2†	0.0864
S	1.23
No. of reflections used in refinement	1064
No. of parameters used	82
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0220P)^2 + 0.1823P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\rm max}$	0.0
$\Delta\rho_{\rm max}$ (e Å^{-3})	0.57
$\Delta\rho_{\rm min}$ (e Å^{-3})	−0.50
Flack parameter	0.00 (9)
Extinction method	None
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C)

* $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

† $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$	$V(CN)$
Si(1)	0.4418 (2)	0.6346 (2)	0.39418 (11)	0.0075 (3)	−4.03
Si(2)	0.63085 (15)	0.7191 (2)	0.06411 (11)	0.0064 (2)	−4.02
O(1)	0.5191 (5)	0.8034 (5)	0.5611 (3)	0.0102 (7)	1.93
O(2)	0.1922 (4)	0.6916 (6)	0.3292 (3)	0.0097 (6)	1.42
O(3)	0.6306 (4)	0.7083 (6)	0.2637 (3)	0.0098 (6)	1.95
O(4)	0.8531 (4)	0.8485 (6)	0.0063 (3)	0.0084 (6)	1.79
O(5)	0.4048 (4)	0.8967 (5)	−0.0003 (3)	0.0087 (7)	2.06
K(1)	0.96799 (13)	0.1875 (2)	0.31378 (9)	0.0146 (2)	−0.71
Li(1)	0.1310 (10)	0.7036 (15)	0.0940 (7)	0.0100 (14)	−1.10

Enraf–Nonius CAD-4T/rotating anode system (60 kV, 100 mA). Accurate lattice parameters were derived from the SET4 setting angles (de Boer & Duisenberg, 1984) of 15 reflections in the range $10 < \theta < 16°$. The intensity data were corrected for Lp but not for absorption. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1985) and subsequent difference-Fourier techniques and refined on F^2 by full-matrix least-squares (*SHELXL*93; Sheldrick, 1993). No observance criterion was applied during this refinement. Neutral scattering factors were taken from *International Tables for Crystallography* (1992, Vol. A). Geometrical calculations and the *ORTEP* plot were carried out with *PLATON* (Spek, 1990). Calculations were performed on a DEC5000 cluster. Data collection and refinement parameters are collected in Table 1.

Hygroscopicity measurements were carried out on a ENET equipment computer-controlled forced air humidity cabinet at 296 K and 60% relative humidity. The weight of the samples was monitored by taking them from the cabinet sealing the containers, weighing them and replacing them until constant weight. The amount of moisture was determined in two steps: from 293 to 378 K by weight loss after overnight drying in a vacuum oven and from 378 to 923 K using a modified coulometric Karl Fischer assaying method. CO_2 absorbance was measured by using a LECO and a Fissons NA1500 NCS analyser.

DTA and TGA coupled with a mass spectrometer showed that all water was released at 923 K, that CO_2 started to evolve at 673 K, reaching a peak value at 973 K, and that besides H_2O and CO_2 no other volatile species evolved up to 1273 K.

3. Results

The atomic positions, equivalent displacement parameters $U_{\rm eq}$ and calculated valence strength V are collected in Table 2, bond lengths and angles in Table 3.* Projections of the crystal structure are shown in Fig. 1 and an *ORTEP* (Johnson, 1965) plot in Fig. 2. The weight gain and analytically determined H_2O and

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* Lists of anisotropic displacement parameters, atomic coordinates, full geometry and structure factors have been deposited with the IUCr (Reference: NA0075). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected geometric parameters (Å, °)*

Silicon coordination			
Si(1)—O(1)	1.628 (3)	Si(2)—O(3)	1.630 (3)
Si(1)—O(3)	1.637 (3)	Si(2)—O(5)	1.657 (3)
Si(1)—O(1$^{\rm i}$)	1.645 (3)	Si(2)—O(5$^{\rm ii}$)	1.642 (3)
Si(1)—O(2)	1.577 (3)	Si(2)—O(4)	1.566 (3)
Potassium and lithium coordination			
K(1)—O(2$^{\rm iii}$)	2.731 (3)	Li(1)—O(4$^{\rm ii}$)	1.896 (7)
K(1)—O(2$^{\rm iv}$)	2.765 (3)	Li(1)—O(4$^{\rm vii}$)	1.901 (7)
K(1)—O(4$^{\rm v}$)	2.984 (3)	Li(1)—O(2)	1.933 (6)
K(1)—O(4$^{\rm vi}$)	3.034 (3)	Li(1)—O(5)	2.070 (7)
K(1)—O(2$^{\rm i}$)	3.121 (3)	K(1)—Li(1$^{\rm iii}$)	3.126 (7)
K(1)—O(3$^{\rm vi}$)	3.070 (3)		
Oxygen coordination			
O(1)—Si(1)	1.628 (3)	O(4)—Si(2)	1.566 (3)
O(1)—Si(1$^{\rm viii}$)	1.645 (3)	O(4)—Li(1$^{\rm ix}$)	1.896 (7)
O(2)—Si(1)	1.577 (3)	O(4)—Li(1$^{\rm iv}$)	1.901 (7)
O(2)—Li(1)	1.933 (6)	O(5)—Si(2$^{\rm ix}$)	1.642 (3)
O(3)—Si(2)	1.630 (3)	O(5)—Si(2)	1.657 (3)
O(3)—Si(1)	1.637 (3)	O(5)—Li(1)	2.070 (7)
Around Si(1)		Around Si(2)	
Si(1)—O(1)—Si(1$^{\rm viii}$)	134.12 (16)	Si(2)—O(5)—Si(2$^{\rm ix}$)	132.31 (16)
Si(1)—O(1$^{\rm i}$)—Si(1$^{\rm i}$)	134.12 (16)	Si(2)—O(5$^{\rm ii}$)—Si(2$^{\rm ii}$)	132.31 (16)
Si(1)—O(3)—Si(2)	134.38 (16)	Si(2)—O(3)—Si(1)	134.38 (16)
⟨Si—O—Si⟩	134.21 (16)		133.00 (16)
O(1)—Si(1)—O(3)	105.35 (15)	O(3)—Si(2)—O(5)	106.46 (13)
O(1)—Si(1)—O(1$^{\rm i}$)	105.43 (13)	O(3)—Si(2)—O(5$^{\rm ii}$)	106.19 (14)
O(1$^{\rm i}$)—Si(1)—O(3)	105.00 (15)	O(5)—Si(2)—O(5$^{\rm ii}$)	107.25 (13)
O(1)—Si(1)—O(2)	114.20 (15)	O(3)—Si(2)—O(4)	111.47 (14)
O(2)—Si(1)—O(3)	114.83 (14)	O(4)—Si(2)—O(5)	113.06 (14)
O(1$^{\rm i}$)—Si(1)—O(2)	111.17 (16)	O(4)—Si(2)—O(5$^{\rm ii}$)	111.99 (14)
⟨O—Si—O⟩	109.35 (15)		109.40 (14)
Around Li			
O(4$^{\rm ii}$)—Li(1)—O(4$^{\rm vii}$)	103.4 (3)		
O(4$^{\rm ii}$)—Li(1)—O(2)	113.0 (4)		
O(4$^{\rm ii}$)—Li(1)—O(5)	100.4 (3)		
O(2)—Li(1)—O(5)	106.0 (3)		
O(4$^{\rm vii}$)—Li(1)—O(5)	112.9 (3)		
O(4$^{\rm vii}$)—Li(1)—O(2)	119.6 (3)		
⟨O—Li—O⟩	109.2 (3)		

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

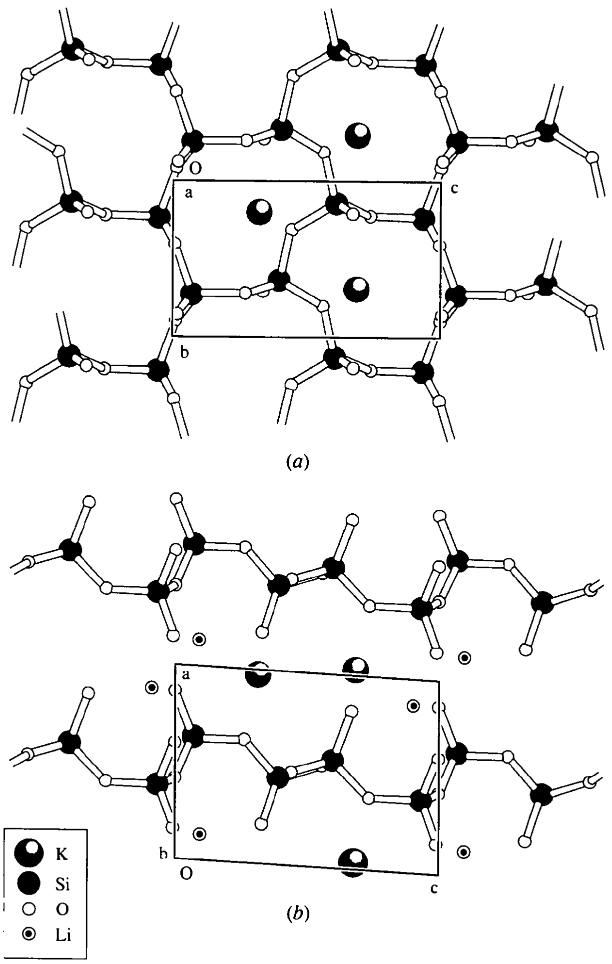

Fig. 1. Projection of the sheet structure of $KLiSi_2O_5$ down (*a*) the *a* axis and (*b*) the *b* axis. Li atoms have been omitted for clarity.

CO_2 concentrations are illustrated in Fig. 3. The precision and accuracy for H_2O analysis is good, the maximum error being 5%; the CO_2 precision is good, but the accuracy is not as good: the percentage error varying between 2 ($K_2O.2SiO_2$) and 56% ($Cs_2O.2SiO_2$).

4. Discussion

4.1. *Comparison of the potassium lithium phyllosilicate structure with that of lithium and caesium lithium phyllosilicate*

4.1.1. *Silica sheet structure*. The silica sheet in potassium lithium phyllosilicate consists of six-membered rings of silica tetrahedra in a chair conformation. This conformation is similar to that encountered in lithium phyllosilicate (Liebau, 1961; Spek, Supèr & de Jong, 1996), with the difference that the chairs are

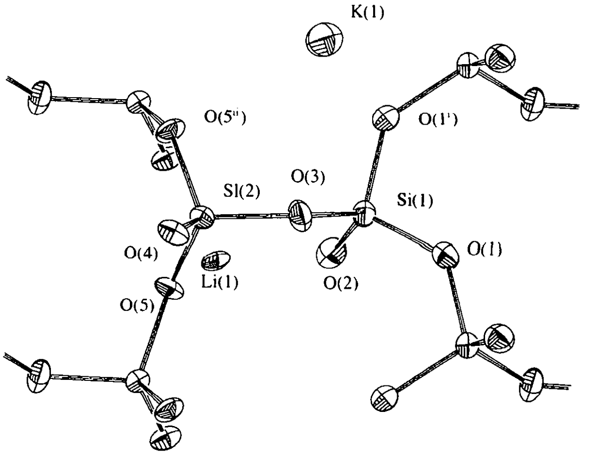

Fig. 2. *ORTEP* (Johnson, 1965) plot drawn at the 90% probability level for $KLiSi_2O_5$. The indicated symmetry symbols are: (i) $1-x, y-\frac{1}{2}, 1-z$; (ii) $1-x, y-\frac{1}{2}, -z$.

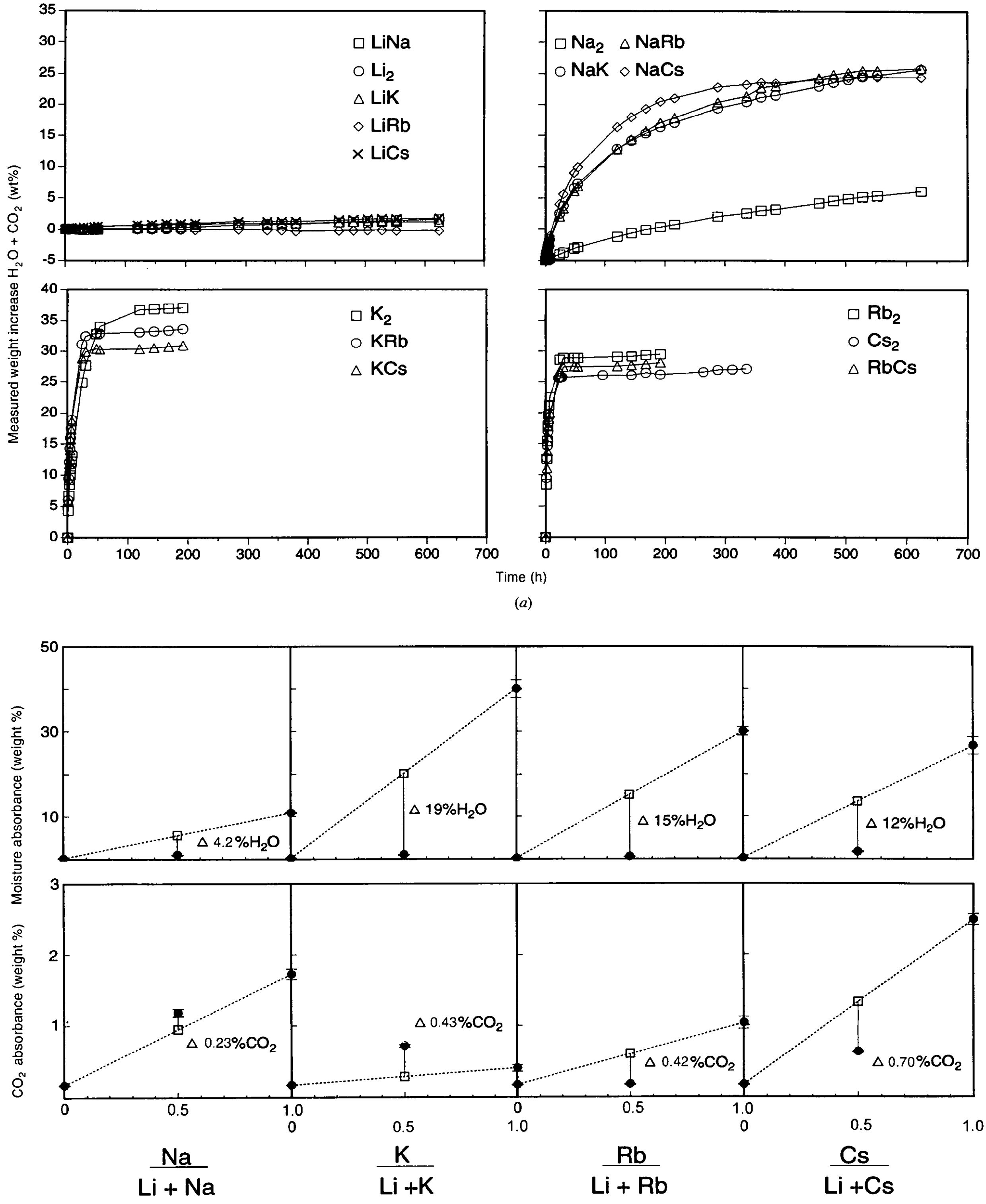

Fig. 3. (*a*) Measured weight increase for the 15 alkali and 1:1 mixed alkali disilicate glasses after exposure in a computer-controlled humidity cabinet to an atmosphere of 60% relative humidity at 276 K. (*b*) Analytically determined H_2O and CO_2 content for the end-member and lithium-containing mixed alkali disilicate glasses after reaching their equilibrium weight increase (60% relative humidity, 276 K). The square boxes indicate the expected linear value, the closed circles the observed. *Δ* gives the deviation from linearity of moisture and CO_2 absorbance in these systems.

symmetric in the latter structure. The result of this asymmetry is that the degree of corrugation of the sheet in the potassium lithium phyllosilicate is less than that in lithium phyllosilicate and the Si—O—Si angle variation substantially smaller. Thus, whereas in stable lithium phyllosilicate two of these angles are 128.7 (3)°, the third being 160.4 (6)° (Spek, Supèr & de Jong, 1996), these three angles cluster in potassium lithium phyllosilicate around 134°, as can be verified by inspection of Table 3.

4.1.2. *Alkali coordination and position with respect to the silica sheet.* The oxygen coordination around lithium is that of a distorted tetrahedron with O—Li—O varying between 100.4 (3) and 119.6 (3)°. Three of the oxygens are non-bridging [O(nbr)], while one is bridging [O(br)]. The oxygen coordination around potassium is sixfold, forming an irregular coordination sphere with five oxygens in one plane with the K atom. Of these five O atoms one is O(br) and the remaining four are O(nbr) atoms, whereas the sixth O atom O(nbr) shows 70° as the smallest angle with respect to the plane. Considering the planar potassium–oxygen linkages as spokes, these are irregularly spaced with respect to one another, the angles between the spokes varying between 70 and 122°.

The position of the Li atoms is indicated in the projection perpendicular to the plane of silicon rings in Fig. 1(*b*). Lithium resides just above and below Si(2) (in the projection down **a**) and hence there is no continuous channel filled with Li atoms. The Li atoms connect the O(nbr) between the layers and hence form the struts which support the silica sheets. In contrast, K atoms reside approximately in the middle of the six-membered rings and form continuous channels throughout the structure. The K and Li atoms lie in a 1.5 Å wide zone parallel to the *bc* plane, as such resembling the alkali-containing layer in a regular mica. Such layering of the alkalis in a relatively narrow zone is not observed in caesium lithium disilicate where caesium forms the channel fill and threefold oxygen coordinated Li atoms again form the struts which separate the silica sheets.

4.1.3. *Hygroscopicity.* The principal purpose behind this study was to assess why glassy mixed alkali disilicates as well as their crystalline congeners show non-linear absorbances of moisture and CO_2 *vis-à-vis* their pure-end members. The phenomenology is clear and represented in Figs. 3(*a*) and (*b*), where the weight increase is illustrated for the five pure alkali and the ten 50–50 mixed alkali disilicate glasses after exposure to a controlled atmosphere of 60% relative humidity at 296 K. Although notoriously difficult to reproduce in detail, these data indicate that all lithium-containing silicates show virtually no weight increase, whereas all other single or mixed alkali silicates do. At issue is how to account for this remarkable role of lithium, which has been noted in a variety of other chemical contexts (Sapse & von R. Schleyer, 1995).

Table 4. *Average valences and their ranges (in parentheses) of oxygen, alkali and silicon in alkali disilicates calculated using the parametrization of Brese & O'Keeffe (1991)*

Compound	⟨O⟩	⟨Alkali⟩		⟨Si⟩	
$Li_2Si_2O_5$	2.14 (2.03; 2.23)	−1.02	–	−4.29	–
$KLiSi_2O_5$	1.83 (1.42; 2.06)	−0.71 (K)	–	−4.03	(−4.02; −4.03)
		−1.10 (Li)	–		
$K_2Si_2O_5$[a]	1.92 (1.85; 2.07)	−1.12	(−0.93; −1.51)	−4.03	(−3.98; −4.09)
$Cs_2Si_2O_5$	2.09 (1.73; 2.22)	−1.03	(−0.99; −1.07)	−3.98	(−3.76; −4.17)
$Cs_{1.33}Li_{0.67}$-Si_2O_5	2.06 (1.85; 2.22)	−1.09 (Li)	–	−4.12	(−4.07; −4.16)
		−0.95 (Cs)	–		

(*a*) Veldman, Spek, Supèr & de Jong (1996).

Table 5. *Cationic field strength, ionic mobility at infinite aqueous dilution, approximate hydration number, and hygroscopicity of end-member glassy alkali disilicates*

	Cationic field strength ($\times 10^{16}$ cm^{-2})	Ionic mobility at infinite dilution[a]	Approximate hydration number[a]	Hygroscopicity glassy $R_2O.2SiO_2$ (R = Li, Na, K, Rb, Cs; mol%H_2O)
Li^+	0.23	33.5	25.3	1.5
Na^+	0.19	43.5	16.6	53.5
K^+	0.13	64.5	10.5	88.2
Rb^+	0.12	67.5	10.0	86.9
Cs^+	0.10	68.0	9.9	87.2

(*a*) Lee (1991).

The hygroscopicity increase for the end-member glassy alkali disilicates varies monotonically with cationic field strength, as most of the physical and chemical properties of alkali-containing salts tend to do. However, such dependencies do not necessarily represent true cause and effect relations as inspection of the data in Table 5 shows. Thus, glassy $Li_2Si_2O_5$ is non-hygroscopic, $Na_2Si_2O_5$ intermediate and $K_2Si_2O_5$, $Rb_2Si_2O_5$ and $Cs_2Si_2O_5$ very hygroscopic, mimicking the trend in decreasing cationic field strength of the constituent alkali ion. However, inspection of Table 5 shows that the hydration number, *i.e.* the approximate number of water molecules surrounding Li^+, is much larger than Cs^+ or in other words that the former cation has a much larger affinity for moisture than the latter. This disagrees with what might have been inferred from our results on glassy alkali disilicates, that increased cationic field strength of the alkali is associated with decreased affinity for moisture. Of course, these considerations pertaining to end-member glassy disilicates do not shed any light on the hygroscopicity of the mixed glassy alkali disilicates.

There is no clear structural reason why potassium lithium phyllosilicate should not be hygroscopic. There are no short K—Li linkages [sum Shannon–Prewitt radii Li^{IV}—K^{VI} 2.25 Å (Shannon & Prewitt, 1969) observed at 3.126 (7) Å], the K atoms do not occur as occluded pockets preventing moisture or CO_2 from reaching them and the structure is not more compact than that of other phyllosilicates, as might be inferred from variation in interlayer spacing. As an approximate measure of this interlayer spacing, approximate because of the extreme corrugation of the silica sheets in some of these compounds, the half-length of the lattice parameter perpendicular to the sheet can be used. This spacing increases from 5.98 Å in non-hygroscopic $KLiSi_2O_5$ (this study) to 5.98 Å in slightly hygroscopic β-$Na_2Si_2O_5$ (Pant, 1968), 7.29 Å in non-hygroscopic $Li_2Si_2O_5$ (Spek, Supèr & de Jong, 1996), 7.73 Å in slightly hygroscopic α-$Na_2Si_2O_5$ (Pant & Cruickshank, 1968) and 9.48 Å in non-hygroscopic $Cs_{1.33}Li_{0.67}Si_2O_5$ (Veldman, Spek, Supèr & de Jong, 1995). Thus, no relation between interlayer spacing and hygroscopicity exists.

One might believe that in hygroscopic systems valences are not completely satisfied and hence some residual binding power remains. Inspection of Table 2 shows that whereas most valences in potassium lithium phyllosilicate are well accounted for, one O(2), a non-bridging oxygen, has in actuality a very low value due to the bonding of this atom to one Si atom and one Li atom only. This statement rings true at least as long as one considers as a strict coordination criterion that no anions can reside in the first coordination sphere around an anion. Thus, around O(2) next to the Si and Li atoms, whose distances are collected in Table 3, three O atoms occur at 2.658 (4), 2.691 (1) and 2.708 (3) Å, before the first K atom at 2.731 (3) Å. Including the contribution of this last cation to the valence of O(2) would result in a value of 1.62 Å, a somewhat more acceptable but still quite low value. One would therefore surmise that this atom might attract moisture from the air. However, such reasoning is clearly faulty since potassium lithium phyllosilicate is not hygroscopic at all. For some recently determined alkali phyllosilicates the calculated valences using our strict coordination criterion are collected in Table 4. Inspection of the values in this table indicate an occasionally fairly large deviation from expected values, which was already observed early on in calculating valences, as discussed by Bragg (1930). For lithium phyllosilicate the valences of the constituent atoms fall within proper bounds and one might argue that this is the reason why this compound is not hygroscopic. In caesium phyllosilicate, the valences of the constituent atoms fall in ranges which are similar to those observed in caesium lithium phyllosilicate. However, in this case the former compound is hygroscopic, the latter not at all. Clearly residual valences are not a discriminating criterion in assessing hygroscopicity of a material.

The most noticeable point in the lithium-containing mixed alkali phyllosilicates is that no atom pairs are formed as has been suggested (Vessal *et al.*, 1992) to explain the up to nine orders of magnitude decrease in electrical conductivity of mixed alkali systems *vis-à-vis* their pure-end members. Rather, the alkalis end-mix with Li atoms residing in one structural site, the other alkali in another site without any clear cut interaction as has been proposed elsewhere (de Jong, Keefer, Brown & Taylor, 1981; Yap, Foster & Elliot, 1995).

Lithium-containing mixed alkali systems remain, therefore, still puzzling and the large synergetic effects in electrical conductivity and hygroscopicity associated with mixed-alkali salts can still not be explained by looking at crystallographically determined structural details. However, the awareness that it exists for all, not only silica based, alkali salts might be of substantial importance in areas where minimizing hygroscopicity is an issue, as for instance in NaI scintillating crystals.

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