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(K$_4$Li$_4$)Al$_8$Ge$_8$O$_{32}$·8H$_2$O: an Li$^+$-exchanged potassium aluminogermanate with the zeolite gismondine (GIS) topology

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The title compound, lithium potassium dialuminium digermanium octaoxide dihydrate, (K,Li)-(Al,Ge)-GIS (GIS is gismondine), is the result of a 50% Li$^+$ exchange into the K-(Al,Ge)-GIS structure. The (K,Li)-(Al,Ge)-GIS structure was determined from a 4 × 4 × 2 μm octahedral single crystal at the ESRF synchrotron X-ray source. The ion exchange results in a symmetry transformation from *I*2/*a* for K-(Al,Ge)-GIS to *C*2/*c* for (K,Li)-(Al,Ge)-GIS. The structural change is due to disordering of K$^+$ ions with Li$^+$ ions along the [001] channel and ordering of water molecules in the [101] channels. The distance between sites partially occupied by K$^+$ ions increases from 2.19 (3) Å in K-(Al,Ge)-GIS to 2.94 (3) Å in (K,Li)-(Al,Ge)-GIS. The Li$^+$ ions occupy positions along the twofold axis at the intersection of the eight-membered-ring channels in a twofold coordination with water molecules. For the four closest framework O^{2-} anions, the Li···O distances are 3.87 (4) Å.

Comment

Zeolites and microporous materials with the gismondine (GIS) structure are characterized by perpendicular double crankshaft chains of tetrahedra. These tetrahedra are connected at all corners, thus forming pore systems that consist of two eight-membered ring (8MR) channels connected by four-membered rings (4MRs) (Baerlocher *et al.*, 2001). The GIS topology has high framework flexibility (Bauer & Baur, 1998; Tripathi *et al.*, 2000; Baerlocher *et al.*, 2001), which allows the accommodation of a wide range of extra-framework cations. This flexibility offers the potential for studying the mechanisms of ion-exchange reactions in the same framework topology using an array of guest species. Previous ion-exchange studies on gismondine-type zeolites include those by Bauer & Baur (1998) and Tripathi *et al.* (2000). Bauer & Baur (1998) exchanged Li$^+$ and K$^+$ ions into crystals of Na-GIS. In the precursor material, the Na$^+$ sites were half-occupied and coordinated to the walls of both 8MR channels. The other half occupancy was attributed to water molecules. Upon Li$^+$ exchange, Li$^+$ ions occupied only one channel at the center of a distorted tetrahedron formed by two framework O^{2-} anions and two water molecules. Upon K$^+$ exchange, K$^+$ ions occupied the centers of the 8MR channels, these sites being previously disordered with water molecules. Tripathi *et al.* (2000) reported the structure of 50% Na$^+$-exchanged K-(Al,Ge)-GIS, in which Na$^+$ and K$^+$ ions are disordered with water molecules and each cation species occupies the center of a separate 8MR channel. K-(Al,Ge)-GIS was chosen for ion-exchange studies because of the well characterized structure of the native material and the unique structure adopted upon ion exchange (Tripathi *et al.*, 2000). The present study presents the first ion-exchange and structural characterization of Li$^+$ in the (Al,Ge)-GIS structure (Fig. 1).

Following the *ex situ* ion exchange, the atomic positions were determined from the collected X-ray diffraction intensities using direct methods. The occupancies of the Al, Ge, K and extra-framework O21 sites were subsequently refined and converged to 1.00 (2) for Al, 1.00 (1) for Ge, 1.00 (4) for O21 and 0.50 (1) for K atoms. The site occupancies of the framework O atoms were not refined, and the H atoms of the water molecule (O21) were not located. In the final difference Fourier map, the highest peak was located 1.63 Å from atom O9 and the deepest hole was located 0.70 Å from the K atom. The refined atomic displacement parameters for the extra-framework species are large, which suggests that these species are highly mobile in the intracrystalline channels. Such displacement parameters are typical for extra-framework species in zeolites (Treacy *et al.*, 1996). An attempt was made to refine the Li site occupancy, but this attempt resulted in either an unacceptably large displacement parameter

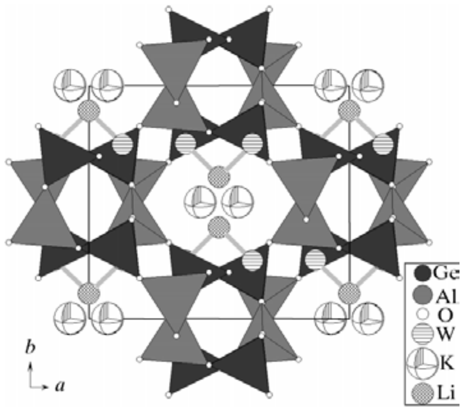

Figure 1
The Li-exchanged gismondine-type structure, viewed along the [001] channel. K—O bonds have been omitted for clarity. Atoms labeled W belong to water molecules.

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($U_{iso} > 0.14$ Å^2) or a low occupancy of approximately 70% (for a fixed $U_{iso} = 0.07$ Å^2), which is insufficient for electroneutrality when combined with the 50% occupancy of the K site. In the final refinement cycles, the Li site occupancy was therefore fixed to 100% for charge balance, which led to reasonable anisotropic U parameters for the K, O21 and Li sites. The displacement ellipsoid for the Li atom is elongated along the [101] direction, suggesting a high ionic conductivity for the Li$^+$ ions, as seen in other Li$^+$-bearing microporous structures (Park *et al.*, 2000).

Magic angle spinning nuclear magnetic resonance (^{6}Li MAS NMR) and thermogravimetric analysis (TGA) measurements were performed to qualitatively confirm the presence of Li and quantitatively determine the number of water molecules in the Li$^+$-exchanged K-(Al,Ge)-GIS structure. The MAS NMR analysis showed a single peak shifted 0.9 p.p.m. from the standard [1 *M* LiCl (aqueous)]. Similar work by Park *et al.* (2002) described the Li$^+$ ions in extra-framework positions in another Li-bearing zeolite as having small peak shifts of between 0.41 and 1.0 p.p.m., which is consistent with our results. The TGA results showed an 8.7% weight loss between 298 and 342.4 K, which agrees with the calculated water content (8.8 wt%) determined from the single-crystal refinement.

The sites occupied by Li$^+$ ions correspond to crystallographic special (4*e*) positions along the twofold axis at the intersection of the [101] and [001] channels. The Li$^+$ ions have a twofold coordination (Fig. 2) with two water molecules (O21) and do not coordinate with the framework O^{2-} anions, since the shortest Li$\cdots$O distances (to four framework O atoms) are 3.87 (4) Å. Similar extra-framework cation environments have been reported by Martucci *et al.* (2003) in modernite, in which the Ca^{2+} ions are only coordinated by water molecules. The shortest distance between K$^+$ sites increases from 2.19 (3) Å in K-(Al,Ge)-GIS to 2.94 (3) Å in (K,Li)-(Al,Ge)-GIS. The K$^+$ ions coordinate to two water molecules (O21) and to three framework O^{2-} anions.

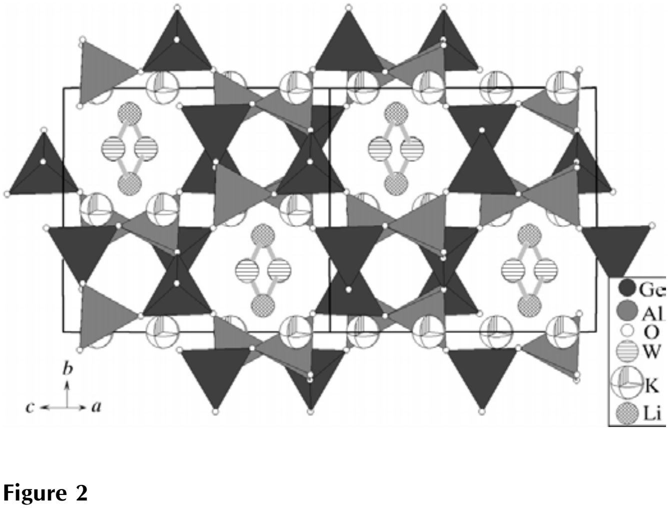

Figure 2
A view along the [101] channel, showing the Li$^+$ ions in twofold coordination with water molecules (W).

The gismondine structure transforms from space group $I2/a$ to $C2/c$ upon 50% substitution of Li$^+$ for K$^+$. The unit-cell transformation is $a = -a' - c'$, $b = b'$ and $c = a'$, where $a/b/c$ and $a'/b'/c'$ refer to the *I*-centered and the *C*-centered unit cells, respectively. The symmetry change is accompanied by a change in T—O—T angles (T = Al and Ge), which range from 135.5 (2) to 136.5 (2)° in the unsubstituted K-(Al,Ge)-GIS structure (Tripathi *et al.*, 2000) but are distorted in the (K,Li)-(Al,Ge)-GIS structure to accommodate the hydrated Li$^+$ ions (Table 1).

Experimental

K-(Al,Ge)-GIS crystals were synthesized according to the method described by Tripathi *et al.* (2000). The crystals were filtered off, washed with deionized water and dried at room temperature. Their sizes ranged from approximately 4 × 4 × 2 to 60 × 60 × 40 µm along the octahedral edges. The synthesized crystals (10 mg) were placed in a 125 ml polypropylene bottle. LiOH (30 ml, 0.01 *M*) in aqueous solution was added as the exchangeable electrolyte. The crystals were agitated gently for 30 h and then removed from the bottle, filtered off and washed with deionized water. A pristine 4 × 4 × 2 µm octahedral crystal was chosen for single-crystal diffraction studies at the ESRF ID-11 beamline. Larger crystals contained cracks and stacking faults which showed as split and streaky spots in the single-crystal diffraction patterns. ^{6}Li MAS NMR measurements were carried out at 29.47 MHz on a CMX-200 spectrometer using a Chemagnetics probe equipped with a 4 mm rotor. The spectrum was recorded using a single pulse experiment with a spin rate of 10.17 (2) kHz and referenced to an LiCl solution (1.0 *M*) at 0 p.p.m. The TGA experiment was performed on a Netzsch STA 449C instrument. Data were collected on a 3.050 (5) mg sample between 298 and 873 K, with a constant temperature ramp of 2 K min^{-1}.

Crystal data

$(K_4Li_4)Al_8Ge_8O_{32}\cdot 8H_2O$
$M_r = 202.64$
Monoclinic, $C2/c$
$a = 14.807$ (1) Å
$b = 9.5404$ (19) Å
$c = 10.394$ (1) Å
$\beta = 134.12$ (2)°
$V = 1054.1$ (4) Å^3
$Z = 8$
$D_x = 2.531$ Mg m^{-3}

Synchrotron radiation
$\lambda = 0.5164$
Cell parameters from 3801 reflections
$\theta = 0.1$–17.7°
$\mu = 3.30$ mm^{-1}
$T = 293$ (2) K
Octahedron, white
4 (1) × 4 (1) × 2 (1) µm

Data collection

Bruker SMART 1500 CCD diffractometer
ω scans
3770 measured reflections
833 independent reflections
821 reflections with $I > 2\sigma(I)$

$R_{int} = 0.073$
$\theta_{max} = 17.7°$
$h = -17 \rightarrow 17$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.076$
$S = 1.07$
833 reflections
79 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 6.3673P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.005 (2)

Table 1
Selected geometric parameters (Å, °).

Ge—O3	1.729 (3)	Al—O1	1.757 (3)
Ge—O2	1.731 (3)	K—O1^{iv}	2.944 (5)
Ge—O4	1.736 (3)	K—O3^{v}	2.947 (5)
Ge—O1	1.753 (3)	K—O4^{iii}	2.969 (5)
Al—O2^{i}	1.739 (3)	K—O21^{vi}	3.145 (6)
Al—O3^{ii}	1.747 (3)	Li—O21^{vi}	2.05 (3)
Al—O4^{iii}	1.751 (3)		
O3—Ge—O2	107.93 (17)	O3^{ii}—Al—O4^{iii}	111.60 (18)
O3—Ge—O4	112.15 (16)	O2^{i}—Al—O1	112.98 (16)
O2—Ge—O4	109.29 (15)	O3^{ii}—Al—O1	108.47 (16)
O3—Ge—O1	105.19 (15)	O4^{iii}—Al—O1	113.40 (15)
O2—Ge—O1	110.00 (16)	Ge—O1—Al	130.56 (19)
O4—Ge—O1	112.14 (15)	Ge—O2—Al^{i}	140.2 (2)
O2^{i}—Al—O3^{ii}	107.66 (16)	Ge—O3—Al^{vii}	138.74 (19)
O2^{i}—Al—O4^{iii}	102.55 (16)	Ge—O4—Al^{iii}	134.5 (2)

Symmetry codes: (i) $-1-x, 2-y, -2-z$; (ii) $\frac{1}{2}+x, \frac{5}{2}-y, \frac{1}{2}+z$; (iii) $-1-x, y, -\frac{3}{2}-z$; (iv) $-\frac{1}{2}-x, \frac{5}{2}-y, -1-z$; (v) $\frac{1}{2}+x, y-\frac{1}{2}, 1+z$; (vi) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (vii) $x-\frac{1}{2}, \frac{5}{2}-y, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ENDEAVOUR* (Crystal Impact, 1999; Putz *et al.*, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1016). Services for accessing these data are described at the back of the journal.

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