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A New Porous Lithosilicate with a High Ionic Conductivity and Ion-Exchange Capacity

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Microporous materials are used in heterogeneous catalysis and for separation technologies in selective ion exchange and gas sorption processes.[1,2] Applications may depend critically on the size and shape of the channels and on the choice and siting of extraframework cations residing inside the voids. These cations can be ion-exchanged to sequester contaminants[3] or impart selectivity over and above that determined by the framework geometry.[4] Therefore, a variety of microporous materials have been investigated in application-oriented research, and the search for new crystalline microporous compounds remains of great interest.

Silicate zeolitic materials have a generalized chemical formula $A^{x+}{}_a[\mathrm{Si}_{1-y}T_y{}^{w+}\mathrm{O}_2]\cdot zM$, where $a = (4 - w)y/x$ is required to balance charges.[5] Species *A* are mono- or divalent exchangeable cations. Framework cation species *T*, with typical valence $w = 3$, are tetrahedrally coordinated by oxygen. The symbol *M* is used for neutral guest species, such as H_2O, that may be occluded in the regularly spaced pores and channels. Conventionally, the ion-exchange capacity, determined by the Si/T ratio, is maximized in alumosilicate zeolites by producing materials with low Si/Al ratio.[6] However, the minimum value obtainable is 1.0, limiting the ultimate number of extraframework cations. Further, most zeolitic frameworks can be prepared only with the Si/T ratio in a very limited range.[7]

Minimizing the valence of the T framework, through use of framework Li, provides an alternative approach to increase the ion exchange capacity. Further, $[LiO_4]$-tetrahedra are more flexible than $[SiO_4]$- or $[AlO_4]$-tetrahedra.[8] $[LiO_4]$ can form strain-free three-membered rings with $[SiO_4]$-tetrahedra.[9] In contrast, only one highly strained material, benitoite ($BaTiSi_3O_9$), contains three-membered rings of $[SiO_4]$. This flexibility allows novel porous frameworks capable of both ion exchange and sorption to be produced.[10] Following this strategy, several new porous lithosilicates have been synthesized.[11] Here we report the structure and properties of a novel microporous lithosilicate, RUB-29 (Ruhr-Universitaet-Bochum, #29), which exhibits the highest ratio of Li to Si (1:4) for any of the open framework structures synthesized so far.

A structural model of RUB-29[12] was obtained from synchrotron single-crystal diffraction intensities by direct methods and Fourier calculations.[13] To confirm Li-siting and to find the extraframework (nontetrahedrally coordinated) Li^+ cations, Rietveld analysis using neutron powder diffraction data was essential.[14] The excellent agreement between the observed and calculated diffraction pattern over the entire 2θ range (Figure 1) confirms the quality of the model.

The structure of RUB-29 consists of two different structural building units: pure $[SiO_4]$- and pure $[LiO_4]$-LLBU's (layer-like building units). The pure silica $[Si_{72}O_{144}]$ building blocks consist of rigid $[SiO_4]$-tetrahedra and there are two such blocks per unit cell. Another LLBU contains exclusively corner- and edge-shared flexible $[LiO_4]$-tetrahedra. Within these building units, all tetrahedral interstitial sites are partially occupied by Li cations, and these $[LiO_4]$-tetrahedra form a body-centered network. A 3-dimensional framework structure is created by connecting these via Li−O−Si linkages. These linkages give rise to two types of unusual structure building units, (Li,Si)-spiro-3,5 and (Li,Si)-spiro-5, that contain three-membered rings of $[LiO_4]$- and $[SiO_4]$-tetrahedra (Figure 2). This is the first report of the silicate (Li,Si)-spiro-3,5 unit. The RUB-29 framework shown in Figure 3 is a 3-dimensional channel system of intersecting 8MR/10MR-10MR-8MR in the [100], [010], and [001] directions, respectively (MR: membered-ring). Within the pores, nonframework Cs and Li cations and water molecules are occluded.

The high degree of isomorphic substitution of Si by Li (Li:Si = 1:4) gives rise to a large negative charge on the framework that must be compensated by a high density of extraframework cations, an essential prerequisite for optimized ion-exchange capacity. The Cs cations within the RUB-29 channel system are readily exchanged with other cations. In preliminary ion-exchange experiments, at least 60% of Cs cations were exchanged by Na. The ^{133}Cs and ^{23}Na MAS NMR spectra indicate that the Na cations replace most of the Cs cations on the larger sites, such as those at the intersections of the 10MR-channels.[15]

Variable-temperature ^7Li MAS NMR experiments were used to probe lithium motion. A gradual broadening and then disap-

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(12) Structure formula, $Cs_{14}Li_{24}[Li_{18}Si_{72}O_{172}]\cdot 14H_2O$.; space group, *I*222; refined lattice parameters, $a = 11.208(1)$ Å, $b = 17.286(1)$ Å, $c = 23.536(1)$ Å; and unit cell volume, $V = 4660(1)$ Å^3.

(13) A single crystal of RUB-29 ($10 \times 10 \times 2\ \mu m^3$) was used for the data collection at the ×3A1 beamline of the NSLS ($\lambda = 0.632$ Å). Using isotropic displacement parameters for Cs, Si, O, and framework Li atoms and refined site occupation parameters of Cs and Li without restrains, the final R_1 value converged to 0.10 ($R_1 = \sum||F_o| - |F_c||/\Sigma|F_o|$) for 5773 reflections [$|F_o| > 4\sigma(|F_o|)$].

(14) The final unconstrained Rietveld-refinement resulted in discrepancy indices: $wR_p = 0.039$, $R(F_2) = 0.024$, and $\chi^2 = 0.9$ [$wR_p = (M/\sum wI_o{}^2)^{0.5}$ with $M = \sum w(I_o - I_c)^2$; $R(F_2) = \sum|F_o{}^2 - SF_c{}^2|/\sum|F_o{}^2|$ with S = scale factor; $\chi^2 = M/(N - P)$, where *N* is the number of observations and *P* the number of variable parameters]. Data were collected using the 32 detector BT-1 neutron powder diffractometer at the NIST NBSR reactor. Measurements were performed under ambient conditions using a Ge(311) monochromator with $\lambda = 2.0783(2)$ Å.

(15) ^{133}Cs, ^{23}Na, and ^7Li MAS NMR experiments were performed with a 5 mm double-resonance Chemagnetics probe on a CMX-360 spectrometer. Operating frequencies were 47.22, 95.23, and 139 MHz, spinning speeds 8, 8, and 10 kHz, and pulse delays were 1, 1, and 5 s respectively for ^{133}Cs, ^{23}Na, and ^7Li. Chemical shifts were referenced against 1 M CsCl, NaCl, or LiCl (0 ppm).

(16) $\sigma = nabq2\omega/(kT)$ where n = concentration of the charge carriers per unit volume, a and b = lattice parameters, q = effective charge of the carriers, ω = hopping frequency, k = Boltzmann’s constant, T = temperature in Kelvin (*Fachlexicon ABC Physik, 1982*; Verlag Harri Deutsch: Thun Frankfurt/M.; Band 1, p 689).

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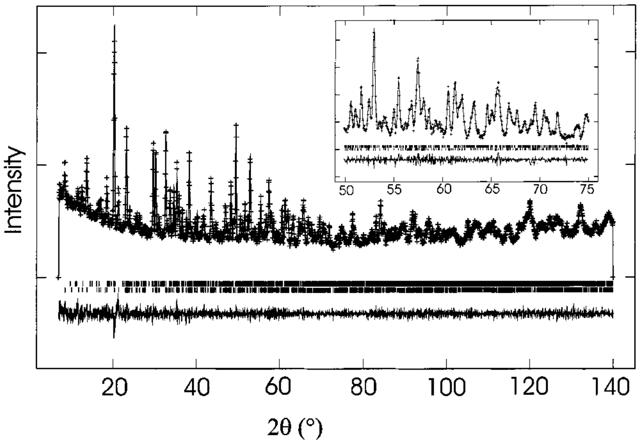

Figure 1. Computed (line) and observed (crosses) diffraction for the neutron data of deuterium-exchanged RUB-29 and the crystallographic model. The upper and lower sets of short vertical lines indicate reflections of the impurity compound RUB-23 and RUB-29, respectively. The lower curve shows the difference between the observed and calculated data. The plot is enlarged in the high angle range $50° < 2\theta < 75°$ to emphasize agreement between the data and the model.

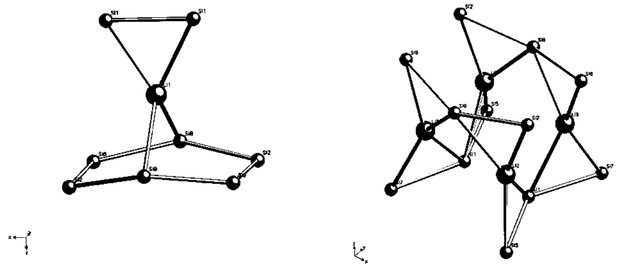

Figure 2. Novel structure building units Li,Si-spiro-3,5 (left) and Li,Si-spiro-5 (right). Small circles indicate the centers of [SiO_4]-tetrahedra, and big circles those of [LiO_4]-tetrahedra. In Li,Si-spiro-3,5, Li is located at the center of one 3MR and two 5MR's of [(Si,Li)O_4]-tetrahedra.

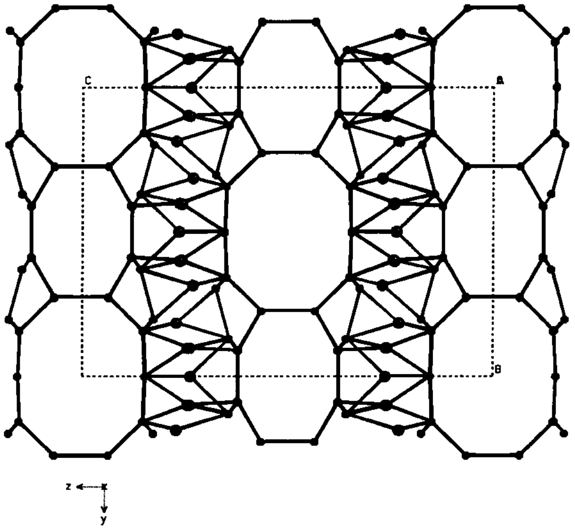

Figure 3. Projection of the RUB-29 framework structure on (100). The centers of each [SiO_4]- (smaller circles) and [LiO_4]-tetrahedron (larger circles) are indicated.

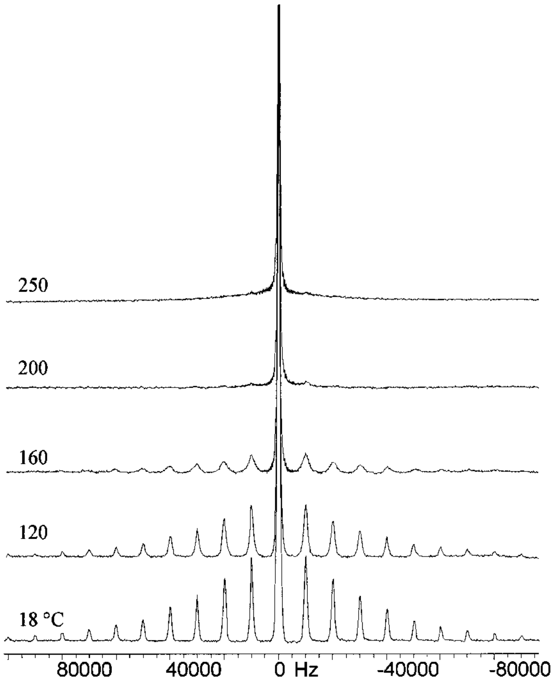

Figure 4. ^{7}Li MAS NMR experiments performed in the temperature range 25 to 250 °C. By 250 °C all spinning sidebands disappear and only the isotropic resonance remains. This suggests that all framework and nonframework Li^+ cations are mobile.

pearance of the spinning sidebands due to the ^{7}Li satellite transitions is seen as the Li^+ hopping frequency approaches first the time scale of the magic angle spinning (160−200 °C) and then the quadrupolar interaction (≥250 °C; Figure 4). Diffraction measurements are also consistent with dynamical disorder of Li cations. Thus, RUB-29 may be an excellent two-dimensional ion conductor. A conductivity $\sigma_{200\ °C}$ of $2 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$ was estimated for lithium cations at 200 °C in the RUB-29 structure based upon the NMR experiments.[16] Conductivity values of the same order of magnitude have been observed in a lithium-stuffed derivative of β-quartz structure, β-eucryptite ($LiAlSiO_4$). This material shows a conductivity of 10^{-5} and $10^{-8}\ \Omega^{-1}\ cm^{-1}$ at 200 °C parallel and perpendicular to [001], respectively, and the one-dimensional ionic conductivity (||[001]) reaches values consistent with superionic conductivity ($>10^{-2}\ \Omega^{-1}\ cm^{-1}$) at temperatures above 500 °C, due to the dynamically disordered Li ions parallel to the *c*-axis.[17] A.C. impedance measurements of RUB-29 are now in progress to determine the temperature dependence of the ionic conductivity and to correlate local probes of motion (NMR) with bulk measurements.

Despite the high degree of Li mobility, RUB-29 is stable to at least 500 °C in a vacuum. The enhanced flexibility of the [LiO_4]-moiety may explain the presence of three-membered rings of [LiO_4]- and [SiO_4]-tetrahedra and the stability of the RUB-29 framework structure. This stability should be contrasted to many zeolitic materials with high aluminum content that lose crystallinity following multiple rehydration and dehydration steps.[18]

The unique framework properties of tetrahedral Li atoms and high ionic conductivity clearly demonstrate that this class of new materials deserves further investigation.

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Supporting Information Available: A table of crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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