Study of Ion-exchanged Microporous Lithosilicate Na-RUB-29 by Using Synchrotron X-ray Single-crystal Diffraction

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Introduction

The recently discovered lithosilicate RUB-29 ($Cs_{14}Li_{24}[Si_{72}Li_{18}O_{172}]\cdot 14H_2O$) possesses a unique open $[Si_{72}Li_{18}O_{172}]$-framework composed of corner-shared $[SiO_4]$- and corner- and edge-shared $[LiO_4]$-tetrahedra [1, 2]. These structural elements are strictly segregated into alternating layerlike building units (LLBUs) that are interconnected to form a 3-D system of channels bounded by 3-, 4-, 5-, 6-, 8-, 9-, and 10-membered rings (MRs), as shown in Fig. 1. Inclusion of $[LiO_4]$ building units in the framework gives rise to a high framework charge, which is balanced by Cs and Li cations in the channels. The exchange of the larger channel-blocking Cs cations for smaller cations represents an important use of these new materials in gas separation and catalysis. There are seven unique positions available for Cs cations (labeled Cs1 through Cs7 in Fig. 1) and four for nonframework Li cations (Li4, Li5, Li7, and Li8) in the channels of as-synthesized RUB-29. Because of the complexity of RUB-29 structure and our desire to obtain accurate atomic structural information, we employed single-crystal diffraction (XSD) methods. Further, because of the small size of the crystals [1] and their decrease in size upon exchange, a third-generation synchrotron source was required for data collection. Here we report on a systematic study of the ion-exchange process of RUB-29.

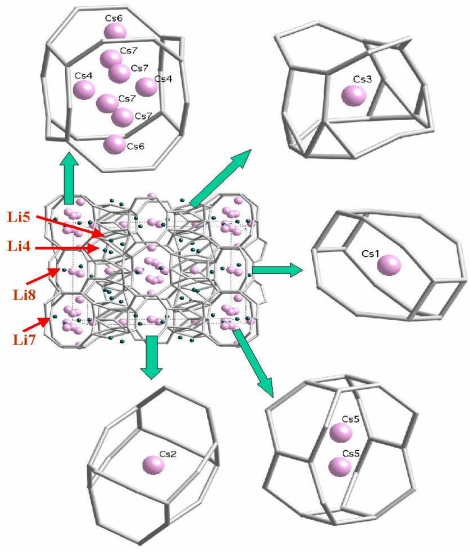

FIG. 1. Location of Cs and Li cations in the structure of as-synthesized RUB-29. Oxygen sites, at the approximate midpoints of the lines, are omitted for clarity. The Si and Li atoms lie at the nodes of the net.

Methods and Materials

A pure RUB-29 sample was made by using the optimized synthesis parameters reported in detail in Refs. 2 and 3. Twenty glass vials with a volume of 3 mL were filled with 5 M NaCl solution, and about 10 mg of RUB-29 crystals were added to each. All were kept at room temperature and were shaken sporadically. From that batch, one vial per day of Na-exchanged RUB-29 crystals was carefully washed with deionized water and dried at room temperature. The samples were designated according to exchange time, with Na1d being a sample of Na-RUB-29 obtained by Na exchanging for one day, Na2d exchanging for two days, and so on.

Collection of the crystallographic data for Na1d, Na5d, Na13d, and Na18d was done at beamline 13-BMD of the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS) at the APS. Each Na-RUB-29 crystal with an edge length between 20 and 30 μm was mounted, and data were collected on a Bruker charge-coupled device (CCD) detector with a graphite monochromator [λ = 0.6199(3) Å]. The crystal is located 3.92 cm from the detector and rotated about 360° continually during the data collection in the $\varpi/2\theta$ scan mode. The integrated reflections were corrected for the absorption effect by using the program SADABS distributed by Bruker Analytical [4]. The crystal structures were solved by direct methods and then refined by difference Fourier calculations with SHELXTL of the Bruker program suite [4].

Results

All single crystal x-ray diffraction (XRD) data for the Na-exchanged samples Na1d, Na5d, Na13d, and Na18d were consistent with the space group of the as-synthesized (native) RUB-29, ***I***222. The chemical composition of each exchanged sample was determined directly from the refinement results. Table 1 summarizes experimental conditions and results for the data collected on each sample.

Table 1. Summary of the results of crystallographic experiments and the structure refinements of Na-RUB-29 [$(Cs,Na,Li)_{38}(Si_{72}Li_{18})\cdot xH_2O$] Na1d, Na5d, Na13d, and Na18d with increasing degree of Na exchange.

Condition	Na1d	Na5d	Na13d	Na18d
Lattice parameter a (Å)	11.216(2)	11.160(2)	11.177(2)	11.156(2)
Lattice parameter b (Å)	17.360(1)	17.264(4)	17.354(6)	17.356(4)
Lattice parameter c (Å)	23.916(5)	23.969(5)	24.203(4)	24.137(5)
Space group	I 2 2 2	I 2 2 2	I 2 2 2	I 2 2 2
Wavelength (Å)	0.6199	0.6199	0.6199	0.6199
Scan mode	ϖ-2θ	ϖ-2θ	ϖ-2θ	ϖ-2θ
Exposure time per frame (s)	5	2	15	10
2θ range (°)	51.83	62.93	51.81	51.95
No. of unique reflections after merging for Fourier	3431	4583	3682	3493
R1 (= Σ| $\|F_o\|$ – $\|F_c\|$ |/Σ$\|F_o\|$) for all unique reflections	0.04	0.16	0.10	0.09
Good of fit ($\chi 2$)*	1.1	1.1	1.6	1.6
No. of Cs, Na, and Li in unit cell	Cs = 6.4 Na = 10.7 Li = 20.9	Cs = 6.4 Na = 10.8 Li = 20.8	Cs = 3.7 Na = 14.1 Li = 20.2	Cs = 1.2 Na = 16.6 Li = 20.2

*$\chi 2 = \Sigma w(|F_o|^2 - |F_c|^2)2/(N - P)$, where N = number of observations, P = number of variable parameters, and w = weight = $1/[\sigma^2(F_o^2) + (0.2\cdot p)^2 + 0.0\cdot p]$ where $p = \text{Max}(F_o^2, 0) + 2\cdot F_c^2)/3$.

With increasing exchange time, the Na cations preferentially replace Cs in the larger sites located at the intersections of the 10MR/10MR/8MR-channels. The smaller Cs sites are then replaced. After 18 d, more than 85% of the Cs in sites Cs2, Cs3, Cs4, and Cs7 was replaced by Na. Only 42% of the Cs cations on Cs1, which is the smallest channel void available for Cs in RUB-29, were exchanged by Na. The Cs5 and Cs6 sites found in the structure of the native material [1, 2] are occupied by neither Na nor Cs in Na-RUB-29. Surprisingly, structural analysis of the single crystal data of Na18d revealed a Li cation site near Cs6.

The occupancy of sites Li4 and Li5 did not change within the precision provided by the structure refinement, indicating that Na^+ does not replace Li^+ at these sites. The occupancy value for the Li7 site, located in 10MR channels, increases continuously from Na1d through Na18d, with most of the Li^+ replaced by Na^+. With increased exchange degree, the distances d(Li7_O) increase, which is consistent with the observation that the Li7 site within Na18d is occupied by more Na cations (and water molecules) than that within Na1d. In the Na-RUB-29 structures investigated so far, we could not find lithium cations in the Li8 site. From neutron powder diffraction data references [1], the site was determined to be a channel Li cation site in an as-synthesized RUB-29 structure. Instead of the Li8 site, a new Li site designated Li8* was found in Na13d and Na18d. This is located about z = +0.5 from the position of Li8 parallel to the c-axis. The occupancy of Li8* (0.6) is similar to that of Li8 in RUB-29.

Discussion

The Na cations can exchange with more than 90% of the Cs cations and 16% of the Li cations without resulting in any changes in the lattice symmetry. Most Li cations within the channels either remain or relocate. Relocation of Li cations onto new sites within the channels was observed after 13 d of ion exchange. The fate of Li in both framework and extra-framework sites during exchange also agreed with results recently obtained by ^{6}Li magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy [3].

The most readily exchanged sites generally have lower bond valence sums [5, 6]. The present work is consistent with ion exchangeability in the complicated channel system, which was predicted in terms of bond valence and accessibility for these Cs and Li cation sites [3]. The successful removal of Cs and its replacement by the smaller Na suggests the interior of RUB-29 may be made available for possible separations.

Acknowledgments

Use of the APS was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. This work was supported by DOE Grant No. DE-FGO2-94ER14466, National Science Foundation (NSF) Grant No. EAR-9906456, and the W. M. Keck Foundation (GSECARS). We acknowledge financial support from NSF and DOE via DMR-0095633.

References

[1] S.-H. Park, J. B. Parise, H. Gies, H. Liu, C. P. Grey, and B. H. Toby, J. Am. Chem. Soc. **122**(44), 11023–11024 (2000).

[2] S.-H. Park, J. B. Parise, and H. Gies, *Proc. of the 13th International Zeolite Conference* (Montpellier, France, July 8-13, 2001); Studies in Surface Sci. and Catalysis **135**, edited by A. Galarneau, F. Di Renzo, F. Fajula, and J. Vedrine (Elsevier Science, 2001).

[3] S.-H. Park, M. Kleinsorge, C. P. Grey, and J. B. Parise, J. Solid State Chem., JSSC2001-0544 (in revision).

[4] Bruker Analytical X-Ray Systems, *SHELXTL for Windows NT® (Version 5.10)* (1998).

[5] I. D. Brown, in *Structures and Bonding in Crystals*, edited by M. O'Keeffe and A. Navrotsky (Academic Press, New York, NY, 1981), Chap. 14.

[6] I. D. Brown and R. D. Shannon, Acta Crystallogr. A **29**, 266-282 (1973).