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Immobilization of Large, Aliovalent Cations in the Small-Pore Zeolite K-Natrolite by Means of Pressure**

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Dedicated to Professor Hi-Soo Moon

Selective ion exchange is one of the fundamental properties of zeolites enabling various environmental and industrial applications.[1] The ion-exchange selectivity of a zeolite is controlled in part by the geometry of the pores and channels through which exchanging cations diffuse and bind via framework oxygen atoms.[2] Most studies on the ion-exchange properties of zeolites have been carried under near-ambient conditions to establish the selectivity series between mono- and divalent cations[1b] and, to a lesser extent, for trivalent cations such as lanthanides and actinides. Due to steric hindrance, however, small-pore zeolites such as natrolite and related fibrous zeolites have not received much attention with regard to ion-exchange applications.[3] The composition of natural aluminosilicate natrolites lie exclusively near the pure sodium form ($Na_{16}Al_{16}Si_{24}O_{80}\cdot 16H_2O$), and nonframework cation substitutions have been known to be feasible for smaller aliovalent cations such as Li^+ and NH_4^+.[4] Li and NH_4 exchange increases the ellipticity of the 8-ring channel by reducing the unit-cell volume by about 2 and 4%, respectively, making these materials less favorable for further ion-exchange applications.

We recently established that natrolite can also incorporate larger cations under ambient conditions by successive replacement of the sodium cations in the channel. Sodium-to-potassium exchange expands the unit-cell volume by about 10%, and even enables further exchange to give rubidium and cesium forms with about 15.7 and 18.5% larger unit-cell volumes, respectively.[5] During this process, the elliptical 8-ring channel transforms progressively into circular shape by rotating the T_5O_{10} subunits perpendicular to the channel axis. Exchange of monovalent by divalent cations such as Ca^{2+} and Sr^{2+} has also been achieved for the K form of natrolite.[6] We have further developed the chemistry of natrolites, since this framework can show auxetic behavior leading to expansion of the channels under pressure, which can be rationalized in terms of a “rotating-squares” model in which the squares are made up of the T_5O_{10} subunits ($T = Al, Si$).[7] An auxetic material has a negative Poisson’s ratio; when it is compressed or stretched, it becomes thinner or thicker perpendicular to the applied force.[8] Recently Grima et al.[9] showed experimentally that Na-natrolite is an auxetic zeolite with negative Poisson’s ratio. This provides an explanation for the reversible superhydration observed in Na-natrolite, whereby water is inserted under pressure (pressure-induced hydration),[10] and the pressure-induced adsorption of small gas molecules such as Ar and CO_2 into Na-natrolite.[7,11] We utilize the auxetic properties of the natrolite framework to exchange under pressure and trap under ambient conditions trivalent cations such as lanthanides, formerly thought to be non-exchangeable, in K-natrolite.

Pressure-induced cation exchange has recently been shown by ex situ high-pressure quenching experiments to be feasible for partially replacing the sodium cations in Na-natrolite with isovalent cesium.[12] Here we show, for the first time, using in situ diffraction and ex situ high-pressure synthesis, that trivalent europium cations can also be trapped in the natrolite framework.

In situ high-pressure cation-exchange experiments were performed with K-natrolite (K-NAT, $K_{16}Al_{16}Si_{24}O_{80}\cdot 14H_2O$) and 1.0 M Eu^{III} nitrate solution sealed inside a diamond-anvil cell (DAC, see Experimental and Supporting Information). Changes in the synchrotron X-ray powder diffraction patterns clearly show reversal of the relative intensities of the (220) and (111) Bragg peaks and the emergence of the (040) and (400) peak intensities above about 1.5(1) GPa after annealing (Figure 1). The pressure-dependent changes in unit-cell volume of K-NAT in an Eu^{III} exchange medium are shown in Figure 2. Initially the unit-cell volume decreases as expected. At about 1.0(1) GPa the sample in the DAC was heated to 80 °C in an oven to promote hydrostaticity. After

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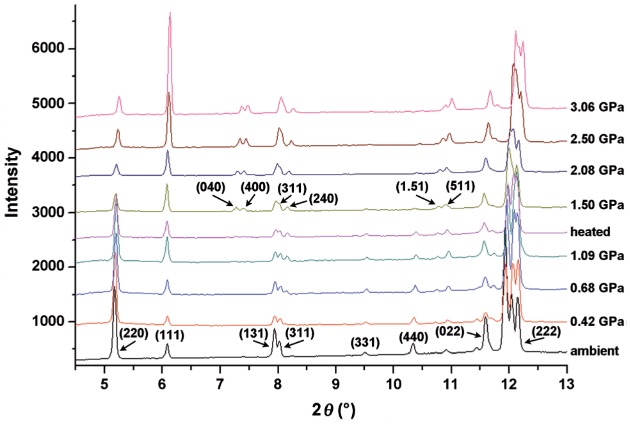


Figure 1. Pressure-induced changes in the synchrotron X-ray powder diffraction patterns measured for K-natrolite under 1.0 M Eu^{III} solution medium by using an imaging plate detector at beamline 5A at PAL. Several Miller indices are shown to emphasize the changes in their relative intensities on Eu^{III} exchange under increasing pressure.

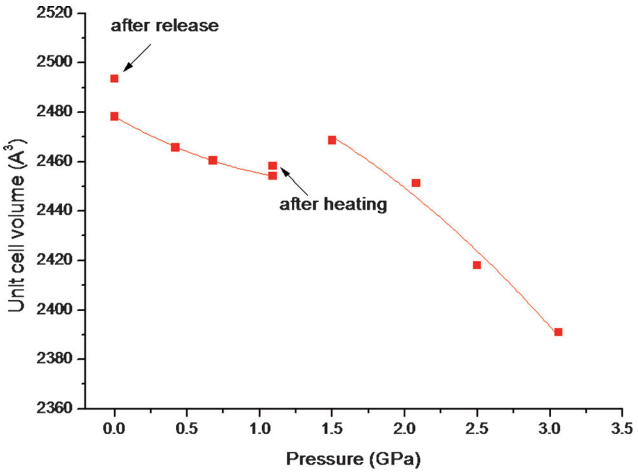


Figure 2. Pressure-dependent changes in the refined unit-cell volume of K-NAT in a 1.0 M Eu^{III} solution used as pressure medium. The estimated standard deviations are smaller than the symbols.

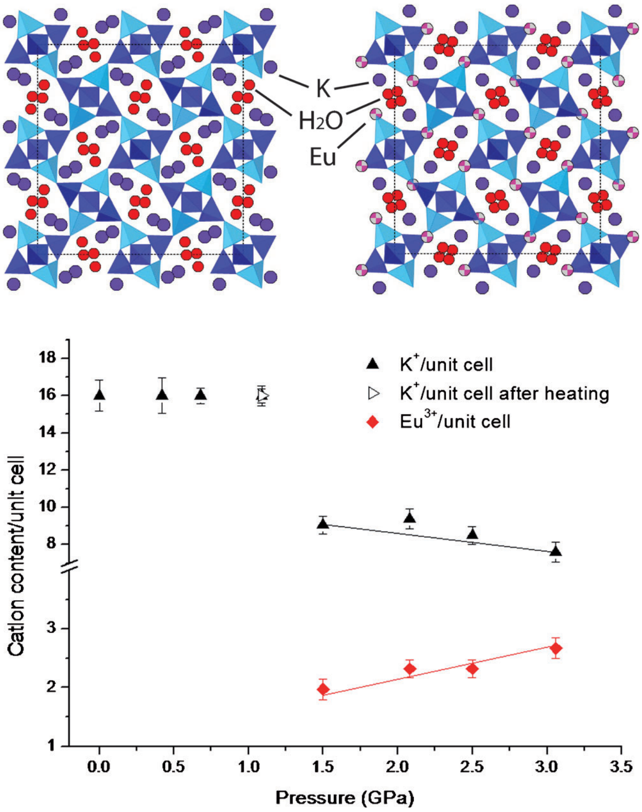


Figure 3. Top: Polyhedral representations of K-natrolite at ambient pressure (left) and under 1.0 M Eu^{III} solution at 1.5 GPa (right), viewed along [001], the chain/channel axis. Note that europium cations partially occupy a site distinct from the sites of potassium cations and water molecules. Dark (light) tetrahedra illustrate an ordered distribution of Si (Al) atoms in the framework. Bottom: Pressure-dependent changes in the refined cation content of K-natrolite in 1.0 M Eu^{III} solution.

heating, a slightly larger unit cell volume was observed at 1.0(1) GPa. On further increasing the pressure to 1.5(1) GPa, the unit-cell volume expanded by about 0.7%, concomitant with the reversal of the (220) and (111) relative peak intensities (Figure 1). Further evidence of chemical exchange under pressure is found in the compression behavior after the pressure-induced expansion. Unlike a "normal" compression observed below 1.0(1) GPa, the pressure derivative of the volume contraction above 1.5 GPa is negative, that is, the unit-cell volume contracts more with increasing pressure. No further discontinuity of the unit-cell volume up to the final pressure of 3.1(1) GPa was observed in the presence of the aqueous 1.0 M Eu^{III} exchange medium.

The structures under ambient conditions and after the pressure-induced expansion at 1.5(1) GPa in the Eu^{III} solution were determined by Rietveld refinements of powder diffraction data (Figure 3). One of the two statistically disordered cation sites along the walls of the major axis of the elliptical channel in the ambient phase migrates to the framework walls of the minor axis at 1.5(1) GPa. This new site partially contains Eu^{III} cations, and their occupancy gradually increases from 1.9(1) per unit cell at 1.5(1) GPa to about 2.7(1) per unit cell at 3.1(1) GPa. Concomitant to the increase in Eu^{III} occupancy, the occupancy of the remaining potassium site decreases, and unit-cell compositions of $K_{9.1(2)}Eu_{1.9(1)}Al_{16}Si_{24}O_{80}\cdot 32\,H_2O$ and $K_{7.7(2)}Eu_{2.7(1)}Al_{16}Si_{24}O_{80}\cdot 32\,H_2O$ at 1.5(1) and 3.1(1) GPa, respectively, result (Supporting Information Table I).

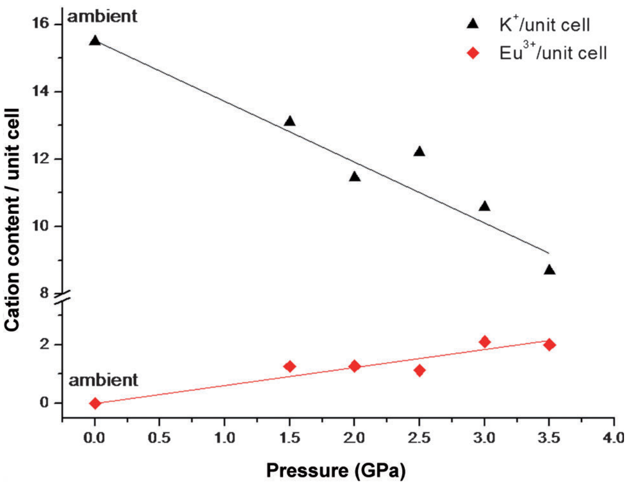
To assess the valence state of the europium cations and provide independent evidence of chemical exchange under pressure, we performed in situ high-pressure micro-Raman experiments with Eu^{III} nitrate solutions of different concentrations as pressure media (see Supporting Information). For the starting exchange mixtures, we observed the characteristic photoluminescent $^5D_0 \rightarrow {}^7F_2$ emission for trivalent europium cations at 614 nm (Supporting Information Figure II-1). Above 1.5(1) GPa, a new Raman band started to appear close to the 4-ring tetrahedral breathing mode at 550 cm^{-1}. Its intensity is found to be proportional to both pressure and Eu^{III} concentration in the solution (Supporting Information Figure II-2). In addition, the breathing mode of the elliptical 8-

ring channel near 420 cm^{-1} did not show any significant shift, consistent with the XRD observation that the degree of Eu^{III} exchange increases with increasing pressure.

As the products recovered from in situ high-pressure exchange were not sufficient for independent chemical analyses, ex situ experiments were performed with a large-volume piston cylinder type high-pressure apparatus (QUICKpress by Depth of the Earth Company, see Supporting Information). Custom-designed Teflon capsules with 3.5 mm diameter and 10 mm height were used to contain the mixture of powder and 1.0 M Eu^{III} solution. To find the optimum conditions for exchange, the first set of experiments were performed by varying the powder-to-solution ratio at fixed pressure and temperature (1.5(1) GPa and 150 °C). Such optimized conditions were then used in two sets of isothermal (at 150 °C) and isobaric (at 3.0(1) GPa) exchange experiments, and the recovered solid products were analyzed by energy-dispersive X-ray analysis (EDX). From the isothermal runs performed at 150 °C, the Eu^{III} exchange level was found to increase with increasing pressure up to 3.5(1) GPa (Figure 4a). The quenched sample from 3.5(1) GPa at 150 °C was found to contain about 2.0 Eu^{III} cations per unit cell, resulting in a composition similar to that observed in situ at 1.5(1) GPa after heating (Supporting Information Table III-1 and Figure 2). However, a significantly higher Eu^{III} exchange level was observed in the isobaric experiments performed at 3.0(1) GPa. The recovered samples show a linear increase of the Eu^{III} exchange concentration with increasing temperature (Figure 4b), and the sample quenched from 3.0(1) GPa and 250 °C contains about 4.7 Eu^{III} cations per unit cell, which is equivalent to over 90% of K^+ being exchanged at high pressure (Supporting Information Table III-1).

In summary, we have demonstrated that, by using pressure and temperature, trivalent europium cations can be immobilized in the small-pore zeolite K-natrolite. Elemental analyses of materials from our high-pressure synthesis established that over 90% Eu^{III} exchange can be achieved at 3 GPa and 250 °C. This result points towards the possibility of designing novel storage media for highly radioactive actinides such as U^{4+} with similar sizes contained in liquid nuclear waste.

(a) 150°C



(b) 3.0 GPa

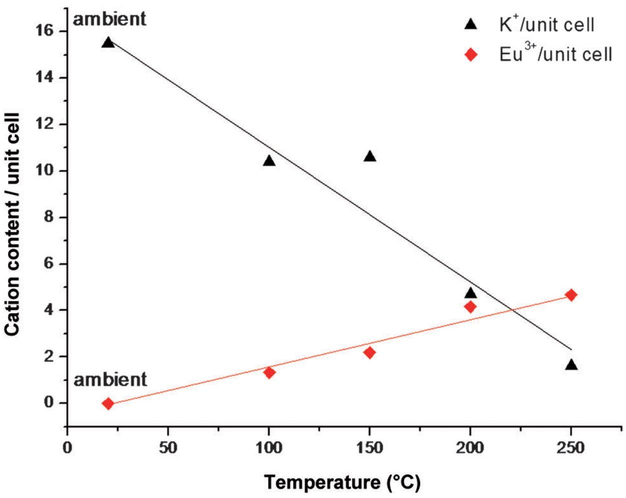


Figure 4. SEM/EDX elemental analysis data for quenched samples from a) isothermal high-pressure runs performed at 150 °C and b) isobaric high-pressure runs performed at 3.0 GPa. Solid lines are guides to the eyes. Estimated standard deviations are smaller than the symbols.

Experimental Section

High-pressure Eu^{III} exchange was monitored in situ by using a Merrill–Bassett-type diamond-anvil cell (DAC)[13] and monochromatic synchrotron X-ray powder diffraction at the 5A-HFMS beamline at Pohang Accelerator Laboratory (PAL). Preparation of the potassium-exchanged natrolite (K-NAT, $K_{16}Al_{16}Si_{24}O_{80}\cdot 14H_2O$) starting material was described in detail by Lee et al.[5] A powdered sample of K-NAT was loaded into a 200 µm-diameter stainless steel gasket chamber together with some ruby chips for in situ pressure measurements. As reference, ambient-pressure data were collected on the dry powder inside the DAC, and then 1.0 M Eu^{III} nitrate solution was used as hydrostatic medium and cation-exchange solution. After loading the liquid pressure medium, the sample chamber was quickly sealed to the initial pressure. The pressure the sample was exposed to in the DAC was measured by detecting the shift in the R1 emission line of the included ruby chips (precision: ±0.05 GPa).[14] The sample was equilibrated for about 30 min in the DAC at each measured pressure. After the 1.0 GPa run, the DAC was heated ex situ at 80 °C in an oven to ensure the sample was hydrostatic. Other details of the in situ experiments and structural refinement procedures are described in the Supporting Information.

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