Pressure-Induced Amorphization of Li-A and Na-A Zeolites

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Introduction

Zeolites are aluminosilicates with well-developed microporous structures that have allowed them to be used extensively as molecular sieves, sorbents, and catalysts in the petroleum industry. The zeolites used in this study (Linde A) consist of an anion framework of silicon and aluminum (Si:Al, ratio 1:1) tetrahedrally bonded to oxygen with Li^+ or Na^+ providing charge balance.[1] The TO_4 (T=Si, Al) tetrahedra are linked together to form a 3-dimensional framework of interconnecting pore and channel structures, which may contain water of hydration. Recently, the electrical properties of Linde A zeolites have been studied as a function of pressure,[2,3] and an anomalous increase in ionic conductivity with pressure up to 1.7-2.2 GPa was observed in Li-A, Na-A and K-A zeolites. Pressure-induced structural changes, or amorphization, of zeolites was suggested as a possible mechanism of this increase in ionic conductivity with pressure. This study was conducted to examine the structural stability of zeolites up to 2.4 GPa and to elucidate the mechanism responsible for the anomalous conductivity increase.

Methods and Materials

Zeolite Na-A (Si/Al =1) was synthesized hydrothermally from a mixture of $2SiO_2:Al_2O_3:5Na_2O:15H_2O$ heated at 80°C for 6 hours. Li-A was prepared through conventional ion exchange methods. The purity and crystallinity of the samples were verified using x-ray diffraction (Philips PW1050 and Rigaku Geigerflex CN2029 powder diffractometer) with Cu Kα and Co Kα radiation, and x-ray fluorescence (Philips PW1450). The zeolites had an atomic ratio of M^+:Al:Si of 1:1:1, where M = Li or Na. Samples were stored for 72 hours, prior to loading into the high-pressure cell, over a saturated solution of NH_4Cl to ensure a maximum degree of hydration. High-pressure experiments were carried out at Argonne National Laboratory, using the Advanced Photon Source (APS) synchrotron. A 250 ton DIA-type high-pressure apparatus installed on beamline 13-BM-D was used to generate the high pressures.[4] Energy-dispersive x-ray diffraction (EDXRD) spectra were collected for 1000 s at each pressure interval with a Ge detector at a fixed 2θ angle of 4.95°. Both samples were contained in a cubic boron nitride (BN) cup and were separated by BN discs. Pyrophyllite was used as the pressure-transmitting medium. Pressure was measured with a NaCl pressure standard, included in two isolated layers in the BN cup, and the Decker equation of state.[5] All experiments were performed at room temperature.

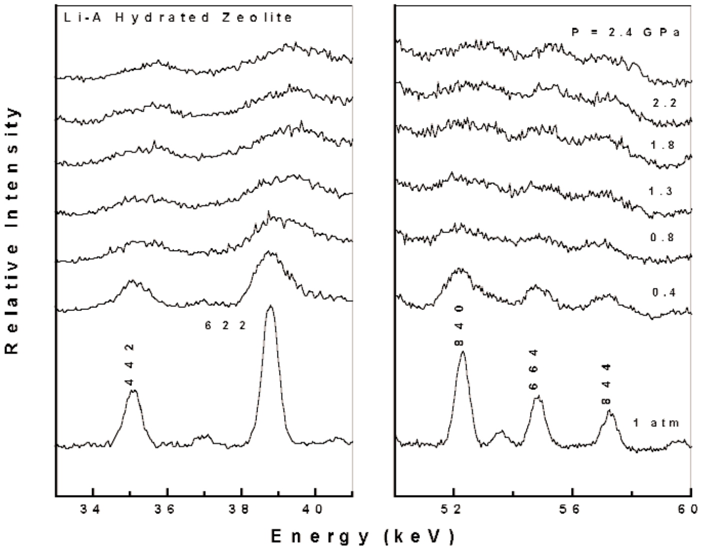

FIG. 1. Energy-dispersive x-ray diffraction patterns for Li-A hydrated zeolite at pressures between 1 atmosphere and 2.4 GPa.

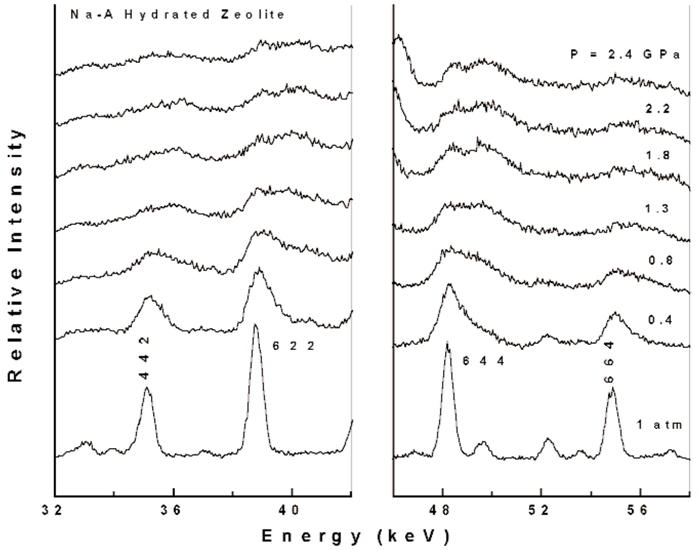

FIG. 2. Energy-dispersive x-ray diffraction patterns for Na-A hydrated zeolite at pressures between 1 atmosphere and 2.4 GPa.

Results and Discussion

Figures 1 and 2 illustrate the EDXRD patterns for hydrated zeolite Li-A and Na-A, respectively, at several pressure intervals up to a maximum pressure of 2.4 GPa. Generally, it can be seen that as pressure increases, the sharp peaks that exist at ambient conditions in both the Li-A and Na-A samples quickly broaden, the intensity drastically decreases, and the peaks shift to higher energy. These changes are most prominent with increasing pressure up to approximately 2.2 GPa. The decrease in peak broadening and reduction in intensity observed for both zeolite Li-A and Na-A with increasing pressure is interpreted as gradual pressure-induced amorphization. Peak 442 for the Li-A and Na-A samples decreases in intensity up to 1.3 GPa, where it then appears as a small hump. Similarly, peak 622 in each sample decreases in intensity until a maximum pressure of 1.8 GPa, where it becomes a small hump. Again, this significant reduction of peak intensity signifies that the sample has undergone, to a large extent, long-range pressure-induced amorphization. The same behavior is observed in all other sample peaks. The 840, 664 and 844 peaks of zeolite Li-A and the 664 peak of Na-A zeolite reduce in intensity and broaden very quickly and essentially flatten at 1.3 GPa, while peak 644 of Na-A appears to persist until a maximum pressure of 2.2 GPa. Generally, it appears as though there is an abrupt decrease in peak intensity accompanied by peak broadening for both zeolites up to a maximum pressure of 2.2 GPa. An infrared (IR) study on the effect of high pressure on Li-A zeolite found an order-to-disorder phase transition at 1.9 GPa, which coincides approximately with the amorphization pressures in this study.[6] The IR work identified a sharp reduction in intensity of the symmetric and asymmetric stretching vibrations with pressure. This suggests that the loss of long-range ordering observed up to 1.3 to 2.2 GPa in this study could be due to the decrease of inter-tetrahedral separation.

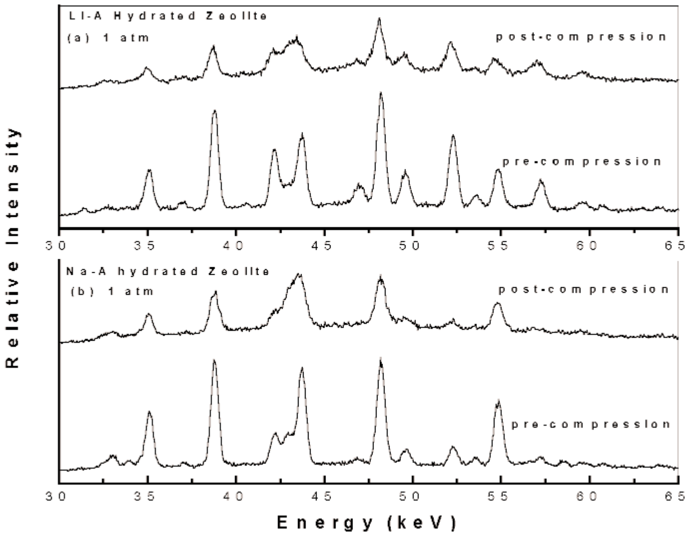

FIG. 3. a) Diffraction patterns for Li-A zeolite at 1 atmosphere for pre- and post- compression to 4.1 GPa. b) Diffraction patterns for Na-A zeolite at 1 atmosphere for pre- and post-compression to 4.1 GPa. Intensities are plotted on the same scale as the 1 atm patterns.

In addition to the pressure-induced amorphization, our observations have shown that the zeolites used in this study have structural memory. Figures 3a and 3b illustrate the EDXRD patterns for zeolite Li-A and Na-A before and after pressurization. The post compression diffraction patterns were taken at 1 atmosphere within the press immediately after unloading. From these figures, it is apparent that upon decompression Li-A and Na-A zeolites regain most of the long-range order that they lost during pressurization. All major peaks initially visible in the ambient diffraction patterns are regained after compression. The reduction in peak intensity observed in the post-compression sample could be due to the x-ray absorption of the extruded pyrophyllite gaskets, which were present during the collection of the post-compression pattern, while they were absent at ambient conditions.

Acknowledgments

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