

In Situ Synchrotron X-ray and Neutron Powder Diffraction Studies of Cd- and Pb-exchanged Zeolite Rho

Y. Lee, J.B. Parise (SUNY, Stony Brook), J.C. Hanson, A. Freitag, and J.Z. Larese (BNL, Chemistry),
B.A. Reisner, B.H. Toby (NIST-NCNR), G.A. Jones, D.R. Corbin (DuPont), and V. Kahlenberg (U. Bremen)

Abstract No. lee1099

Beamline(s): X7B

Description of the cation relocations, observed as a function of temperature in several ion-exchanged samples of zeolite rho, is presumed to be purely temperature-driven [1]. The nature of the negative thermal expansion, exhibited by these materials in the vicinity of these transitions, has remained unclear [2]. We have found that the observed cation relocations and framework contractions are derived by dehydration processes [3]. *In situ* time-resolved synchrotron X-ray and neutron powder diffraction studies were performed on Cd- and Pb-exchanged rho. Rietveld refinements using these data indicated that the negative thermal expansion and cation relocations occur as water molecules bound to these cations are removed from the D8R building unit and that Cd and Pb undergo different rearrangements by migrating from the single 8-ring (S8R) to the single 6-ring (S6R) and double 8-ring (D8R) sites, respectively. These reaction pathways are reversible upon cooling in air, but not in vacuum, demonstrating that water is an important agent in the cation relocations and framework contraction/expansion. *In situ* Kr loading into the α -cages of the fully dehydrated, centric ($Im\bar{3}m$) Cd-rho showed that Kr atoms occupy the D8R, S8R and S6R sites without major changes in cation distribution. Subsequent exposure of the Kr-loaded material to atmosphere resulted in complete desorption of Kr. Further hydration caused a transition to the full-hydrated, centric cubic structure via a transient acentric ($I43m$) cubic phase, possibly during the relocation of Cd from the S6R back to the S8R site. The role of water in these materials studied here is so far known to be unique since other absorbates, such as methanol and CO, did not cause any significant changes in cation and framework positions.

Acknowledgments: The authors thank the NSF for financial support (Grant DMR 97-13375). Research carried out in part at the NSLS at BNL is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, Office of Basic Energy Sciences (Grant DE-AC02-98CH10886 for the X7B beamline).

References: [1] J.B. Parise, D.R. Corbin, and L. Abrams, *Microporous Mater.*, 1995, 4, 99. [2] A. Bieniok and W.H. Baur, *J. Solid State Chem.*, 1991, 90, 173. [3] B.A. Reisner, Y. Lee, J.C. Hanson, G.A. Jones, J.B. Parise, D.R. Corbin, B.H. Toby, A. Freitag, J.Z. Larese, and V. Kahlenberg. (in press) *J. Chem. Soc. Chem. Commun.*

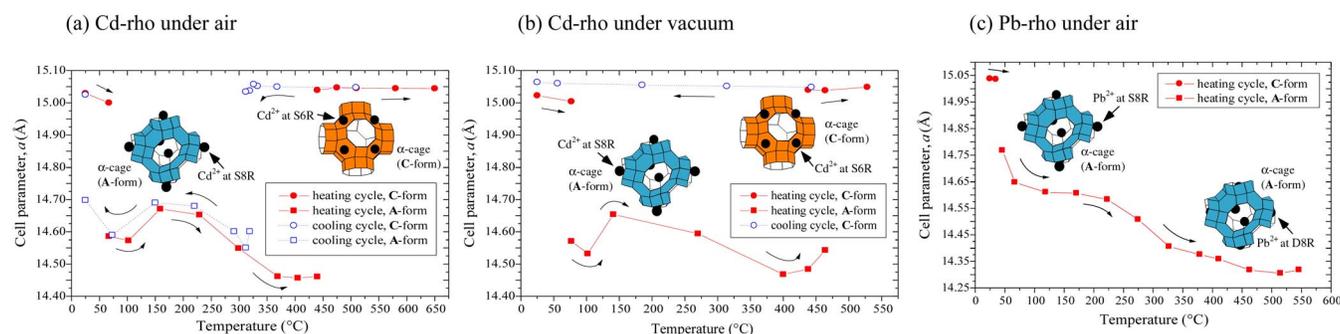


Figure. The cell parameter of (a) Cd-rho heated under air, (b) Cd-rho heated under vacuum and (c) Pb-rho heated under air. Schematic diagrams illustrate the α -cages of the C- and A-forms and the siting of Cd²⁺ and Pb²⁺. (Vertices represent tetrahedrally coordinated Al or Si. Oxygen atoms are omitted for clarity).