Physical Properties and the Role of Defects

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Pressure-mediated crystal-fluid interactions in natural erionite-K

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Abstract Text: Investigating the behaviour at high pressure of crystalline compounds with a microporous structure, e.g. zeolites, has experienced a boosted interest in the last two decades, especially due to the *P*-induced intrusion of molecules and ions into the structural nano-cavities from the *P*-transmitting fluids [1]. Zeolites have a consolidated history of technological and industrial applications, but the understanding of these *P*-induced phenomena may further expand their utilizations, opening the way for new routes for tailoring functional materials. In this study, we have investigated the behaviour of the natural zeolite erionite when compressed in non-penetrating and potentially penetrating fluids: i.e. those fluids made by molecules having a kinetic diameter that may allow their *P*-mediated adsorption into the zeolite structural cavities.

Erionite is a zeolite with a wide chemical variability in Nature, expressed as solid solutions among three end-members: erionite-Ca, erionite-Na and erionite-K.

Our sample, classified as erionite-K, has an average chemical formula: $K_{2.31}Na_{0.02}Ca_{2.15}Mg_{0.69}Ba_{0.04}Sr_{0.02}Al_{9.00}Si_{27.19}O_{72}\cdot 18.66(H_2O)$. Erionite crystal structure is characterized by the presence of large cages (23-hedron, called “erionite-cage”), superposed along the *c* axis, hosting most of the extra-framework population.

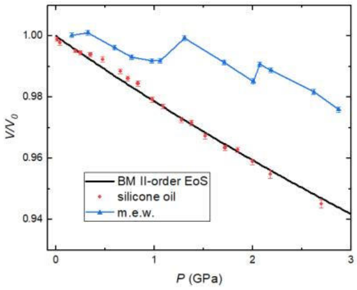
We have conducted experiments by single-crystal X-ray diffraction under *in-situ* high-pressure conditions at the Xpress beamline of the Elettra Synchrotron, using an ETH-type diamond anvil cell (DAC) and ruby as *P*-calibrant. We have performed two *P*-ramps using different *P*-transmitting media: the first one using the non-penetrating silicone oil, up to 2.60(5) GPa, and the second one with the potentially penetrating methanol:ethanol:H_2O = 16:3:1 (hereafter *mew*) mixture, up to 4.97(5) GPa. Using the EoSFit7c software, the *P-V* data obtained by the silicone oil ramp were fitted by a II order Birch-Murnaghan equation of state, yielding the following refined isothermal bulk modulus $K_{V0} = 44(1)$ GPa ($\beta_{V0} = K_{V0}^{-1} = 0.0227(5)$, where β_{V0} is the bulk volume compressibility).

P-V data from the *mew* ramp (Fig. 1) show a significant decrease in compressibility, which unambiguously suggests the (irreversible) *P*-induced intrusion of H_2O (and possibly alcohols) molecules. The adsorption seems to occur in three different steps, approximately around 0.2, 1.2 and 2 GPa. This behaviour is somehow surprising if we consider that the magnitude of the intrusion process is comparable with that of synthetic SiO_2-ferrierite [2] and $AlPO_4$-5 [3] zeolites, but in this case has been observed in a natural sample of erionite, with structural cavities filled by extraframework population.

Further experiments with different classes of potentially penetrating fluids will allow a full understanding and constraints of the *P*-induced adsorption phenomena in erionite.

Fig. 1: High-pressure evolution of the normalized unit-cell volume of natural erionite-K, compressed in mew (blue triangles) and silicone oil (red spheres). Silicone oil data are fitted by II-order Birch-Murnaghan equation of state (black line).

Image 1:



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[2] Lotti P, Arletti R, Gatta GD, Quartieri S, Vezzalini G, Merlini M, Dmitriev V, Hanfland M (2015) Micropor. Mesopor. Mater. 218, 42-54.
[3] Lotti P, Gatta GD, Comboni D, Merlini M, Pastero L, Hanfland M (2016) Micropor. Mesopor. Mater. 228, 158-167.