Monovalent Cation-Exchanged Natrolites and Their Behavior under Pressure. A Computational Study

Abstract:
Recently natrolite was shown to be an auxetic material that is able to exchange extra-framework Na+ cations with other mono-, di-, and trivalent cations. Under pressure up to several GPa, these cation-exchanged natrolites undergo superhydration and/or phase transformations in the cation-water arrangement. Using density functional theory we studied in silico the ion exchange in natrolites. First we optimized the structures of Li+-, Na+-, K+-, Rb+-, and Cs+-exchanged natrolites at ambient conditions and compared the resulting lattice energies to that of the hypothetical H-form of natrolite. Of all natrolites, the smallest formal exchange energy was found for Na-NAT, in agreement with the natural occurrence of this material. Then we modeled the effect of pressure on Na-, Rb-, and Cs-natrolites, addressing (i) the incorporation of water ligands into the zeolite framework, accompanied by an increase in volume; and (ii) the changes in the cation-water arrangement within the zeolite pores. The computational models reproduce reasonably well the critical pressure, at which these phenomena occur, and, in the case of Cs-NAT, point toward a cation displacement model for its structural transition under pressure.