COMPRESSIONITY AND CRISTAL FLUID INTERACTIONS IN SI FERRITE

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Introduction

The interest on the high-pressure (HP) behaviour of zeolites significantly increased during the last decade. The growing number of studies allowed the recognition of complex and variable responses to the applied pressure1,2: a wide compressibility range, a remarkable structural flexibility and the relevant influence played by the framework (topology, cation ordering etc.) and extraframework components on the HP behaviour. Beside the intrinsic properties of the open-framework compounds, a significant number of experiments have been devoted to the high-pressure interactions between zeolites and the P-transmitting medium, as the so-called P-induced over-hydration: i.e. the P-induced penetration of H2O molecules into the structural voids3. The P-driven penetration of molecules is not limited to H2O, several “pore-penetrating” P-transmitting media may be involved in this process.

In this light, pressure may be applied not only to explore the elastic and structural properties of zeolites, but also as a tool to drive changes of these properties: e.g. improving the efficiency in the field of heterogeneous catalysis, favoring the access of reactants and products to/from the catalytically active sites; modifying the physical-chemical properties through irreversible phase transitions; or for the engineering of technological materials through irreversible molecules intrusion.

In this study, we explore (by both single-crystal and powder synchrotron X-ray diffraction) the high-pressure behaviour and crystal-fluid interactions of a synthetic siliceous matrix with ferrierte topology [Si-FER: Si36O72], using a number of penetrating and non-penetrating pressure-transmitting media.

Materials and experimental methods

The single crystals and powders used have all been selected from the same starting sample of synthetic pure Si-ferrierte (Si36O72). The in-situ high-pressure single-crystal (SC) and powder X-ray diffraction experiments have been performed at the ID09A and BM01-Swiss-Norwegian beamslines at ESRF (Grenoble), respectively, using diamond anvil cells. Four different P-transmitting media have been used for both SC and powder experiments: non-penetrating silicon oil and potentially penetrating methanol:ethanol:H2O=16:3:1 mix (m.e.w.), ethylene glycol (egl) and 2methyl-2propen-1ol (mpo).

Results and discussion

The HP-study of Si-FER compressed in silicon oil evidenced the remarkable flexibility of this framework: a first displacive phase transition was observed from the orthorhombic Pmmn to the monoclinic P12/n1 space group at ~ 0.7 GPa. A second displacive phase transition, involving a significant unit-cell volume contraction, was observed at ~ 1.24 GPa from the P12/n1 to the P21/n11 space group (through an intermediate P-1 structure, “type-II” transition according to Christy4). The high-P P21/n11 polymorph was found to be stable at least up to 3.00(7) GPa, whereas - upon pressure release - the starting Pmmn structure was fully recovered. The three polymorphs were found to share a virtually identical bulk elastic behaviour, being their average volume compressibility βv: 0.051(4), 0.056(9) and 0.055(3) GPa3, respectively. The structure deformation is governed by the tilting of the tetrahedra around the shared oxygen hinges. The bulk V-contraction is mainly accommodated, after