First observation of a pressure-induced reconstructive phase transition in zeolites

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A special area of high pressure research is the study of ordered porous solids. Unlike dense materials, their structures present empty volumes, resulting in low framework densities. The most remarkable examples of inorganic crystalline microporous solids are zeolitic materials, composed of silicon oxide and/or other elements like Al, B, Ti or Ge (called T-atoms), where T appears in a tetrahedral coordination. These tetrahedra are arranged in such a way that they form well-defined channels and cavities of molecular dimensions, and have a broad range of applications in catalysis, separation and adsorption processes.

Previous studies found that, under high pressures, tilting of $TO_{4/2}$ tetrahedra has relatively low energy barriers, while shortening of T-O distances requires higher energies. So, at relatively low pressures, distortions are due to inter-tetrahedra tilting around bridging oxygen atoms, which act as structural 'hinges' [1]. In this process, zeolites usually undergo a reversible transition in which they are converted into low density amorphous phases. However, further compression leads to a high density amorphous phase that does not revert back to the original zeolite, suggesting a transition between amorphous solids (polyamorphism) in which some T-O bonds are broken and new T-O linkages are formed [2]. Despite of the number of high-pressure experiments performed on porous solids, the formation of any new zeolite has never been reported. So, it has been claimed that reconstructive phase-transitions, with a change in topology between crystalline phases, do not occur in tetrahedral SiO_2-polymorphs, as feldspars and zeolites [1,2]. However, contrary to this claim, we found for the first time a pressure-induced irreversible solid-to-solid transition between zeolitic structures. In this case, the pure silica analogue of zeolite A (ITQ-29) was transformed into a new topology (named ITQ-50).

ITQ-29 (having LTA structure) combines the simplest zeolite structure (cubic symmetry, one silicon and three oxygen as independent positions) and a very high stability. So, it was chosen for this study, using silicon oil as pressure transmitting medium, which is too large for penetrating into the void channels of the structure. ITQ-29 undergoes two transformations in the range between atmospheric pressure and 6 GPa, being identified a new phase, but no amorphization occurs. The first phase transformation was observed at 1.2 GPa, being fully reversible and ITQ-29 is recovered after pressure release. However, the second transformation, at around 3.2 GPa, is non-reversible, producing a new material named ITQ-50. Unfortunately, the low resolution of the *in situ* DAC experiments precluded the complete structural analysis of ITQ-50 and only the cell parameters were obtained from the diffraction patterns. Then, a large volume Paris-Edinburgh cell with a mixture of Fluorinert as transmitting medium was employed for recovering enough sample of ITQ-50 to perform additional lab XRD measurement. This new pattern allowed solving the crystal structure of ITQ-50. The parent ITQ-29 and the resulting ITQ-50 materials are different zeolites. The main differences are i) the number of independent Si sites (one in ITQ-29, four in ITQ-50), and ii) their connectivities. A comparison of their structures, together with theoretical calculations, allowed understanding the transformation mechanism.

As a conclusion, it can be said that we have undoubtfully evidenced for the first time that zeolites could be transformed into different zeolitic topologies by the effect of pressure, leading from the pure silica zeolite A (ITQ-29) to the new zeolite ITQ-50.

References

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